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(54) Title: AN ORGANIC LIGHT EMITTING DEVICE CONTAINING A PROTECTION LAYER

(57) Abstract

The present invention is directed to organic light emitting devices comprised of a heterostructure for producing electroluminescence, wherein the heterostructure includes a protection layer between a hole transporting layer and an indium tin oxide anode layer. The hole injection enhancement layer may be comprised of 3,4,9,10–perylenetetracarboxylic dianhydride (PTCDA), bis(1,2,5–thiadiazolo)–p–quinobis(1,3–dithiole) (BTQBT), or other suitable, rigid organic materials. The present invention is further directed to methods of fabricating such devices, wherein the devices may include alternative combinations of materials for each of the layers included in the devices.

AN ORGANIC LIGHT EMITTING DEVICE
CONTAINING A PROTECTION LAYER

5   **FIELD OF THE INVENTION**

The present invention is directed to organic light emitting
devices comprised of a protection layer between the hole
transporting layer and the ITO anode layer.

10

BACKGROUND OF THE INVENTION

Organic light emitting devices (OLEDs) are light emitting
devices that are comprised of several layers, in which one of
the layers is comprised of an organic material that can be

15   made to electroluminesce by applying a voltage across the
device, *C.W. Tang et al., Appl. Phys. Lett 51, 913 (1987)*.
Certain OLEDs have been shown to have sufficient brightness,
range of color and operating lifetimes for use as a practical
alternative technology to LCD-based full color flat-panel

20   displays (S.R. Forrest, P.E. Burrows and M.E. Thompson, Laser
Focus World, Feb. 1995). Furthermore, since many of the
organic thin films used in such devices are transparent in the
visible spectral region, they allow for the realization of a
completely new type of display pixel in which the red (R),

25   green (G), and blue (B) emission layers are placed in a
vertically stacked geometry to provide a simple fabrication
process, a small R-G-B pixel size, and a large fill factor.

A transparent OLED (TOLED) which represents a significant step

30   toward realizing high resolution, independently addressable
stacked R-G-B pixels has been reported in International Patent
Application Nos. PCT/US95/15790 and PCT/US97/02681. Such
TOLEDs are disclosed to be capable of having greater than 71%
transparency when turned off and of emitting light from both

35   top and bottom device surfaces with high efficiency
(approaching 1% quantum efficiency) when the device is turned
on. The TOLED uses transparent indium tin oxide (ITO) as the
hole-injecting electrode and a Mg-Ag-ITO layer for electron-
injection. A device was disclosed in which the Mg-Ag-ITO

40   electrode was used as a hole-injecting contact for a second,

different color-emitting OLED stacked on top of the TOLED.
Each device in the stacked OLED (SOLED), which is comprised of
multiple vertically stacked layers, was independently
addressable and emitted its own characteristic color through
5 the transparent organic layers, the transparent contacts and
the glass substrate, allowing the device to emit any color
that could be produced by varying the relative output of the
red and blue color-emitting layers.

10 Thus, publication of PCT/US95/15790 provided disclosure of an
integrated OLED where both intensity and color could be
independently varied and controlled with external power
supplies in a color tunable display device. As such,
PCT/US95/15790 illustrates a principle for achieving
15 integrated, full color pixels that provide high image
resolution, which is made possible by the compact pixel size.
Furthermore, relatively low cost fabrication techniques, as
compared with prior art methods, may be utilized for making
such devices.
20

Devices whose structure is based upon the use of layers of
organic optoelectronic materials generally rely on a common
mechanism leading to optical emission. Typically, this
mechanism is based upon the radiative recombination of a
25 trapped charge. Specifically, organic light emitting devices
comprise at least two thin organic layers separating the anode
and cathode of the device. The material of one of these
layers is specifically chosen based on the material's ability
to transport holes (the "hole transporting layer" or "HTL") and
30 the material for one of the other layers is specifically
selected according to its ability to transport electrons (the
"electron transporting layer" or "ETL"). With such a
construction, the device can be viewed as a diode with a
forward bias when the potential applied to the anode is higher
35 than the potential applied to the cathode. Under these bias
conditions, the anode injects holes (positive charge carriers)
into the hole transporting layer, while the cathode injects

electrons into the electron transporting layer. The portion
of the luminescent medium adjacent to the anode thus forms a
hole injecting and transporting zone while the portion of the
luminescent medium adjacent to the cathode forms an electron
5   injecting and transporting zone. The injected holes and
electrons each migrate toward the oppositely charged
electrode. When an electron and hole localize on the same
molecule, a Frenkel exciton is formed. Recombination of this
short-lived state may be visualized as an electron dropping
10   from its conduction potential to a valence band, with
relaxation occurring, under certain conditions, preferentially
via a photoemissive mechanism. Under this view of the
mechanism of operation of typical thin-layer organic devices,
the electroluminescent layer comprises a luminescence zone
15   receiving mobile charge carriers (electrons and holes) from
each electrode.

The materials that produce the electroluminescent emission are
frequently the same materials that function either as the
20   electron transporting layer or as the hole transporting layer.
Such devices are referred to as having a single
heterostructure. Alternatively, the electroluminescent
material may be present in a separate emissive layer between
the hole transporting layer and the electron transporting
25   layer in what is referred to as a double heterostructure.

In addition to having the emissive material present as the
primary material in the electron transporting layer or in the
hole transporting layer, the emissive material may also be
30   present as a dopant that is contained within a host material.
Materials that are present as host and dopant are selected so
as to have efficient energy transfer between the host and
dopant materials. It is desirable for OLEDs to be fabricated
using materials that provide electroluminescent emission in a
35   relatively narrow band centered near selected spectral
regions, which correspond to one of the three primary colors,
red, green and blue so that they may be used as a colored

layer in an OLED or SOLED. It would be desirable, in
particular, to be able to select these compounds from classes
of compounds in which the emission may be varied by
selectively varying the substituents or by modifying the
5   structure of the base compound that produces emission. In
addition, these materials need to be capable of producing
acceptable electrical properties for the OLED. Furthermore,
such host and dopant materials are preferably capable of being
incorporated into the OLED using starting materials that can
10   be readily incorporated into the hole transporting layer or
electron transporting layer using convenient fabrication
techniques.

Demonstration of efficient electroluminescence from vacuum
15   deposited molecular organic light emitting devices has
generated interest in their potential application for emissive
flat panel displays. To be useful in low cost, active matrix
displays, device structures which are integratable with pixel
electronics need to be demonstrated. A conventional OLED is
20   grown on a transparent anode such as ITO, and the emitted
light is viewed through the substrate, complicating
integration with electronic components such as silicon-based
display drivers. It is therefore desirable to develop an OLED
with emission through a top, transparent contact. A surface-
25   emitting polymer-based OLED grown on silicon with a
transparent ITO and a semitransparent Au or Al top anode has
been demonstrated, *D.R. Baigent, et al., Appl. Phys. Lett. 65,
2636 (1994); H.H. Kim, et al., J. Lightwave Technol. 12, 2107
(1994).*

30

A similar integration of molecular OLEDs with silicon was
achieved using a tunneling SiO_2 interface, Kim et al. The
tunneling interface, however, increases the device operating
voltage, and can be avoided in structures such as for the
35   recently reported transparent TOLEDs, *V. Bulovic, et al.,
Nature 380, 29 (1996). G.Gu, Et al., Appl. Phys. Lett. 68,
2606 (1996),* which can, in principle, be grown on a silicon

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substrate. The TOLED anode, however, forms the electrode
contact which is in direct contact with the substrate, "the
bottom contact", whereas for display drivers employing n-
channel field effect transistors (NFETs), such as amorphous
5   silicon NFETs, it would be desirable for the bottom contact of
the OLED to be the cathode. This would require fabricating
inverted OLEDs (IOLEDs), that is, devices in which the order
of placing the sequence of layers onto the substrate is
reversed. For example, for a single heterostructure OLED, the
10   electron-injecting cathode layer is deposited onto the
substrate, the electron transporting layer is deposited on the
cathode, the hole transporting layer is deposited on the
electron transporting layer and the hole-injecting anode layer
is deposited on the hole transporting layer.
15

Fabrication of such IOLEDs, thus requires that the ITO anode
layer be sputter-deposited directly or indirectly onto
relatively fragile organic thin films. Since the ITO layer is
typically deposited using conventional sputtering or electron
20   beam methods so as to produce layers having a thickness from
about 500 Å up to as much as 4000 Å, it is desirable that
these layers be deposited at the highest deposition rates
possible so as to reduce the time necessary to prepare such
layers. For example, it has been found that while the ITO
25   layer may be deposited at a rate of up to 50-100 Å per minute,
or more, whenever the ITO layer is deposited on a bare
substrate. However, the deposition rate may be only about 2-5
Å/minute, if the ITO is deposited directly onto an organic
layer or onto a Mg:Ag surface that is typically deposited over
30   several organic layers. Since the organic layers are highly
vulnerable to damage when subjected to the beam of high energy
particles that are used at the higher ITO deposition rates,
higher deposition rates can cause substantial damage to the
underlying organic layers, thus causing unacceptably large
35   deterioration in the overall performance of the OLED.
Whenever the ITO layer of an OLED is deposited onto such
fragile organic surfaces, it would be desirable if the ITO

layer could be deposited at substantially higher deposition
rates than have been possible until now.

In addition, it would be desirable if the hole injection
5   characteristics of the hole injecting layer could be improved.
It has been shown that copper phthalocyanine (CuPc) can serve
as an efficient hole injection layer in conventional OLEDs,
*S.A. VanSlyke et al., Appl. Phys. Lett 69, 2160 (1996) and
U.S. Pat. No. 4,720,432* and it had previously been established
10 that 3,4,9,10-perylenetetra-carboxylic dianhydride (PTCDA) is
an efficient hole transporting layer, *P.E. Burrows et al.,
Appl. Phys. Lett. 64, 2285 (1994), V. Bulovic et al., Chem.
Phys. 210, 1 (1996); and V. Bulovic et al. Chem. Phys. 210, 13
(1996); respectively.* Furthermore, the use of PTCDA in a
15 photodetector structure with an ITO electrode deposited on the
film surface, *F.F. So et al., IEEE. Trans. Electron. Devices
36, 66 (1989)*, has previously demonstrated that this material
can withstand sputter-deposition of ITO with minimal
degradation to its conducting properties.
20

Conventional displays, including LCD (liquid crystal) and
conventional OLED (organic light emitting device) displays,
have the additional disadvantage of not being well suited for
viewing under bright ambient light. As illustrated in Fig.
25 21, light R emitted from a bright light source L, such as the
sun, is reflected from one or more layers (primarily the
metallic layers) of a conventional display D. The reflected
light R interferes with the ability of a viewer V to view
information bearing light I generated by the display D,
30 thereby reducing the perceived contrast of the image generated
by the display D. A need, therefore, exists for an OLED
display with improved contrast which can be viewed under
bright ambient light conditions.

SUMMARY OF THE INVENTION

The present invention is directed to OLEDs, and a method of
fabricating such OLEDs, that comprise a heterostructure for
producing electroluminescence wherein the heterostructure

5 includes a layer, between the hole transporting layer and the
ITO anode layer, that protects the underlying organic layers
from damage during the ITO sputter deposition process.

One of the features of the present invention is that the

10 protection layer may be used in OLEDs not only for protection
of the underlying organic layers, but the protection layer may
also serve as a hole injection enhancement layer. Examples of
preferred embodiments of the present invention, in which the
protection layer may also function as a hole injection

15 enhancement layer as disclosed in U.S. Serial No. 08/865,491,
filed May 29, 1997, include PTCDA or related arylene-based
compounds.

The present invention is further directed toward an improved

20 method of preparing the ITO layer of an OLED wherein, during
the course of preparing the ITO layer, the deposition rate is
increased from a relatively low initial deposition rate to a
substantially higher deposition rate after the depositing ITO
layer has reached a sufficient thickness such that damage to

25 the underlying layers is prevented. More specifically,
another aspect of the present invention is directed to a
vacuum deposition process in which the initial deposition rate
is increased by a factor of about five- to ten-fold after a
layer thickness of about 50 Å to about 200 Å is reached.

30 Still more specifically, this aspect of the present invention
is directed to a process in which the initial deposition rate
is about 2-5 Å/minute and the final deposition rate is at
least about 50-60 Å/minute.

35 The present invention is still further directed to a high
contrast, transparent organic light emitting device (TOLED)
display wherein the contrast of the display is improved by
minimizing the amount of light reflected from the display.

This is accomplished by the use of a display with a TOLED
structure and by the arrangement of a low-reflectance absorber
behind the TOLED display. TOLEDs have substantially
transparent conducting layers and as such do not reflect light

5   as do the metallic conducting layers of conventional OLEDs.
The low-reflectance absorber arranged behind the TOLED display
acts to absorb the light which passes through the TOLED
display. The majority of the light incident on the TOLED
display is absorbed by the low-reflectance absorber, with very

10   little of the incident light reflected back to the viewer.
This configuration provides improved contrast of the image
displayed by the display. The display of the present
invention also exhibits improved contrast for images of
different colors.

15

The present invention is further directed to OLEDs comprised
of host and dopant compounds which in combination may be used
to produce emission in a relatively narrow band centered near
the saturation wavelength of one of the primary colors.

20

Further objectives and advantages of the present invention
will be apparent to those skilled in the art from the detailed
description of the disclosed invention.

25   **BRIEF DESCRIPTION OF THE DRAWINGS**
Fig. 1 shows a representative IOLED for a single
heterostructural device.

Fig. 2 shows the forward bias current-voltage (I-V)
30   characteristics of 0.05 mm IOLEDs with PTCDA and CuPc
protective cap layers (PCLs), which function as hole injection
enhancement layers, and of a device with no PCL.

Fig. 3 shows the luminescence intensity vs. current (L-I) of
35   the IOLEDs in Fig. 2.

Fig. 4 shows the I-V characteristics of the shape of the EL

emission spectra of IOLEDs with hole injection enhancement layers as compared to that of conventional Alq_3-based OLEDs not having the hole injection enhancement layer.

5   Fig. 5 shows the current vs. voltage of an OLED with and without a 60 Å PTCDA layer between an ITO anode layer and an NPD hole transporting layer.

Fig. 6 shows a cross section of an OLED containing an ITO
10 layer prepared in two stages, the first stage being prepared using a low ITO deposition rate and the second stage being prepared using a substantially higher ITO deposition rate.

Fig. 7 shows how the resistivity of 1000 Å ITO layers
15 deposited on glass with an Ar flow of 200 ("standard cm^3/minute) and at a pressure of 5 mTorr and at 45 W of RF power varies as a function of the O_2 flux.

Fig. 8 shows how the absorption of 1000 Å thick ITO layers
20 deposited at 45 W of RF power varies as a function of wavelength and as a function of O_2 flux (for an Ar flow of 200 sccm, a pressure of 5 mTorr, a rate of 0.8 Å/sec and onto a glass substrate).

25 Fig. 9 shows how the I-V characteristic of a TOLED made using the higher ITO deposition rates (as shown by the small open circles) compares with the I-V characteristic of a TOLED for which the ITO layer was prepared entirely at the slower ITO deposition rate (dashed line).
30
Fig. 10 shows a representative OLED for a single heterostructural device.

Fig. 11 shows the photoluminescence (PL) spectra of
35 aluminumtris(5-hydroxy-quinoxaline), aluminum tris(5-hydroxy-quinoline) and gallium bis(5-hydroxy-quinoxaline).

Fig. 12 shows the electroluminescence spectra of OLEDs
containing an emissive layer of aluminumtris(5-hydroxy-
quinoxaline) with and without the inner salt of a bisphenyl-
squarilium compound of formula III as a dopant.

5

Fig. 13 shows the I-V characteristics of aluminumtris(5-
hydroxy-quinoxaline) with and without the inner salt of a
bisphenyl-squarilium compound of formula VI as the dopant.

10   Fig. 14 shows the photoluminescent spectra of the host
compounds Alq_3 and Alx_3 as compared with the absorbance spectra
of the dopants: the inner salt of a bisphenyl-squarilium dye
("BIS-OH") an indigo dye compound and a fullerene compound, C_{60}.

15   Fig. 15 shows the photoluminescent spectra of the dopant
compounds in solution, the inner salt of a bisphenyl-
squarilium dye ("BIS-OH") (in CH_2CI_2), an indigo dye compound
(in DMSO) and C_{60} (in toluene).

20   Fig. 16 shows the electroluminescent spectra of TPD-Alq_3/C_{60}
devices as a function of increasing C_{60} concentration in the
host Alq_3 material.

Fig. 17 shows the electroluminescent spectra of TPD-Alq_3/(the
25   bisphenol-squarilium dye of formula XI) devices as a function
of the bisphenol-squarilium dopant concentration in the Alq_3
host material.

Fig. 18 shows the electroluminescent spectra of TPD-Alx_3/(the
30   bisphenol-squarilium dye of formula XI) devices as a function
of the bisphenol-squarilium dopant concentration in the host
Alx_3 material.

Fig. 19 shows the electroluminescent spectrum of the TPD-Alx_3/
35   indigo dye compound device with a 1.7% indigo dye compound
concentration.

Fig. 20 shows representative compounds according to formula XIII.

Fig. 21 shows a conventional display device under bright
5   ambient light conditions.

Fig. 22 shows a high contrast TOLED display, in accordance with the present invention, under bright ambient light conditions.
10

Fig. 23 is a cross-sectional view of a first embodiment of a high contrast TOLED display, in accordance with the present invention.

15   Fig. 24 is a cross-sectional view of a second embodiment of a high contrast TOLED display, in accordance with the present invention.

Fig. 25 is a cross sectional view of a stacked light emitting
20   device, in accordance with a first embodiment of the present invention.

Fig. 26 is a cross sectional view of a stacked light emitting device, in accordance with a second embodiment of the present
25   invention.

Fig. 27 is a cross sectional view of a stacked light emitting device, in accordance with a third embodiment of the present invention.
30

Fig. 28 is a cross sectional view of an inverted stacked light emitting device, in accordance with an embodiment of the present invention.

35   Fig. 29 shows an OLED with a distributed Bragg reflector structure.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention will now be described in detail for
specific preferred embodiments of the invention, it being
understood that these embodiments are intended only as
5   illustrative examples and the invention is not to be limited
thereto.

The OLEDs of the present invention are comprised of a
heterostructure for producing electroluminescence which may be
10   fabricated as a single heterostructure or as a double
heterostructure. The materials, methods and apparatus for
preparing the organic thin films of a single or double
heterostructure are disclosed, for example, in U.S. Patent No.
5,554,220, which is incorporated herein in its entirety by
15   reference. As used herein, the term "heterostructure for
producing electroluminescence" refers to a heterostructure
that includes, for a single heterostructure, in sequence, a
hole injecting anode layer, a hole transporting layer, an
electron transporting layer, and a cathode layer. An
20   additional layer or layers may be present between one or more
of the sequential pairs of these layers. For example, for a
double heterostructure, a separate emissive layer is included
between the hole transporting layer and the electron
transporting layer.
25
Either the anode layer or the cathode layer may be in contact
with a substrate and each electrode is connected to electrical
contacts which are capable of delivering a voltage across the
device causing it to produce electroluminescence from an
30   electron transporting layer, a hole transporting layer or a
separate emissive layer. If the cathode layer is deposited on
the substrate, the device may be referred to as having an
inverted OLED (IOLED) structure. An inverted structure may
also be referred to as an "OILED" structure. If the
35   heterostructure for producing electroluminescence is included
as part of a stacked OLED (SOLED), one or both of the
electrodes of an individual heterostructure may be in contact

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with an electrode of an adjacent heterostructure.
Alternatively, dependent on the circuitry used to drive the
SOLED, an insulating layer may be provided between the
adjacent electrodes of the OLEDs in the stack.

5

The single or double heterostructures as referred to herein
are intended solely as examples for showing how an OLED
embodying the present invention may be fabricated without in
any way intending the invention to be limited to the
10   particular materials or sequence for making the layers shown.
For example, a single heterostructure typically includes a
substrate which may be opaque or transparent, rigid or
flexible, and/or plastic, metal or glass; a first electrode,
which is typically a high work function, hole-injecting anode
15   layer, for example, an indium tin oxide (ITO) anode layer; a
hole transporting layer; an electron transporting layer; and a
second electrode layer, for example, a low work function,
electron-injecting, metal cathode layer of a magnesium-silver
alloy, (Mg:Ag) or of a lithium-aluminum alloy, (Li:Al). In
20   the preferred embodiments of the present invention, the order
of these layers may be reversed or inverted, such that the
cathode layer is in direct contact with the substrate.

Preferred materials that may be used as the substrate in a
25   representative embodiment of the present invention include, in
particular, glass, transparent polymers such as polyester,
sapphire or quartz, or substantially any other material that
may be used as the substrate of an OLED.

30   Preferred materials that may be used as the hole-injecting
anode layer in a representative embodiment of the present
invention include, in particular, ITO, $Zn-In-SnO_2$ or SbO_2, or
substantially any other material that may be used as the
hole-injecting anode layer of an OLED.

35

Preferred materials that may be used in the hole transporting
layer in a representative embodiment of the present invention

- 13 -

include, in particular,
N,N'-diphenyl-N,N'-bis(3-methylpheny)1-1'biphenyl-4,4'diamine
(TPD), 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (α-NPD)
or 4,4'-bis[N-(2-naphthyl)-N-phenyl-amino]biphenyl (β-NPD).

5

Preferred materials that may be used as the electron
transporting layer include, in particular,
tris-(8-hydroxyquinoline)-aluminum (Alq$_3$) and carbazole.

10 Preferred materials that may be used as the separate emissive
layer, if present, include, in particular, dye-doped Alq$_3$, or
substantially any other material that may be used as the
separate emissive layer of an OLED.

15 The insulating layer, if present, may be comprised of an
insulating material such as SiO$_2$, SiN$_x$ or Al$_2$O$_3$, or
substantially any other material that may be used as the
insulating material of an OLED, which may be deposited by a
variety of processes such as plasma enhanced chemical vapor
20 deposition (PECVD), electron beam, etc.

The OLEDs of the present invention may also include doped
layers such as disclosed in *S.A. VanSlyke et al., Appl. Phys.
Lett 70, 1665 (1997) and Tang et al., J. Appl. Phys. 64, 3610
25 (1989)*, which are incorporated herein by reference.

The OLEDs of the present invention have the advantage that
they can be fabricated entirely from vacuum-deposited
molecular organic materials as distinct, for example, from
30 OLEDs in which some of the layers are comprised of polymeric
materials. Polymeric materials typically require solvent-
based methods such as spin coating. Vacuum deposition
methods, rather than solvent-based deposition of polymeric
materials, are particularly suitable for use in fabricating
35 the OLED's of the subject invention since such methods permit
integration of all the vacuum deposition steps into a single
overall sequence of steps for fabricating the OLED. Such

methods, thus, do not require the use of solvents or the need to remove air sensitive layers from a vacuum chamber, such that the layers will be exposed to ambient conditions. A vacuum-deposited material is one that can be deposited in a
5   vacuum having a background pressure less than one atmosphere, preferably about 10^{-5} to about 10^{-11} torr.

Although not limited to the thickness ranges recited herein, the substrate may be as thin as 10 µm(micrometer), if present
10 as a flexible plastic or metal foil substrate, such as aluminum foil, or substantially thicker if present as a rigid, transparent or opaque, substrate or if the substrate is comprised of a silicon-based display driver; the ITO anode layer may be from about 500 Å (1 Å = 10^{-8} cm) to greater than
15 about 4000 Å thick; the hole transporting layer from about 50 Å to greater than about 1000 Å thick; the separate emissive layer of a double heterostructure, if present, from about 50 Å to about 200 Å thick; the electron transporting layer from about 50 Å to about 1000 Å thick; and the metal cathode layer
20 from about 50 Å to greater than about 100 Å thick, or substantially thicker if the cathode layer includes a protective silver layer and is opaque.

Thus, there are substantial variations in the type, number,
25 thickness and order of the layers that are present, dependent on whether the device includes a single heterostructure or a double heterostructure, whether the device is a SOLED or a single OLED, whether the device is a TOLED or an IOLED, whether the OLED is intended to produce emission in a
30 preferred spectral region, or whether still other design variations are used.

The present invention is, however, directed in particular to substantially any type of OLED structure in which a protection
35 layer is present between the hole transporting layer and the anode layer. More specifically, the present invention is directed toward OLEDs that include a protection layer that

functions as a protective cap layer (PCL) for reducing ITO
sputtering damage to the underlying organic layers during
fabrication of the OLEDs. The present invention is further
directed to the OLEDs having the enhanced hole injection

5   efficiency properties observed for OLEDs containing such a
protection layer. The enhanced hole injection efficiency is
characterized by having a higher injected current at a given
forward bias, and/or a higher maximum current before device
failure. A "hole injection enhancement layer" is, thus, a

10   layer that may be characterized as a layer that produces a
current that is at least about 10% higher, typically about 50-
100% higher or still higher, than a similar device that lacks
such an additional layer. Such layers are believed to provide
improved matching of the energy levels of the adjacent layers

15   in a manner that results in enhancement of hole injection.

The protection layer, which may also function as a hole
injection enhancement layer, may be formed, for example, by
deposition of a phthalocyanine compound or of 3,4,9,10-

20   perylenetetracarboxylic dianhydride (PTCDA):

bis(1,2,5-thiadiazolo)-p-quinobis(1,3-dithiole) (BTQBT), or
other suitable, rigid organic materials, such as shown by the

25   following compounds:

1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA);

where R = H, alkyl or aryl;

5

where R = H, (1,4,5,8-naphthalenetetracarboxdiimide);

10   where R = CH₃, (N,N'-dimethyl-1,4,5,8-
     naphthalenetetracarboxdiimide);

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where R = H, alkyl or aryl;

where R = H, (3,4,9,10-perylenetetracarboxylic diimide);

5

where R = CH$_3$, (N,N'-dimethyl-3,4,9,10-perylenetetracarboxylic diimide);

10   having a CA index name, bisbenzimidazo[2,1-a:1',2'-b']anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-10,21-dione;

having a CA index name, bisnaphth[2',3':4,5]imidazo[2,1-a:2',1'-a']anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-10,21-dione;

5   having a CA index name, bisbenzimidazo[2,1-b:2',1'-i]benzo[lmn][3,8]phenanthroline-8,1-dione;

having a CA index name,
10   benzo[lmn]bisnaphth[2',3':4,5]imidazo[2,1-b:2'1'-I][3,8]phenanthroline-9,20-dione.

A substituted derivative of any one of these perylene, naphthalene, isoquinoline, phthalocyanine, or phenanthroline
15   based compounds, or family of compounds, may also be used while remaining within the scope and spirit of the present invention.

In one of the preferred embodiments, the cathode is deposited
20   as the bottom layer on the substrate onto which the inverted OLED is deposited. Such an inverted OLED has the advantage that it can be fabricated entirely from vacuum-deposited molecular organic materials as distinct, for example, from OLEDs in which some of the layers are comprise of polymeric
25   materials, which cannot be readily deposited using vacuum deposition techniques. While a protective layer was typically not necessary in inverted polymer-containing OLEDs since the glass transition temperature (T_g) of polymer materials is

typically much higher and, thus, more resistant to damage
induced by ITO sputtering, than the T_g of molecular (non-
polymeric) organic materials, such inverted polymer-containing
OLEDs cannot be readily fabricated using the vacuum deposition
5   technology that is readily available for preparing OLEDs. The
protective cap layer is typically comprised of a crystalline
organic layer that protects the underlying hole conducting
material from damage incurred during sputter deposition of the
ITO anode.

10

The present invention is, thus, directed to OLEDs having
organic layers that can be fabricated entirely from vacuum-
deposited materials. Moreover, the present OLEDs are
comprised of vacuum-deposited molecular organic materials that
15   contain a crystalline organic layer that may serve not only to
protect the underlying hole transporting material from damage
incurred during sputter deposition of the ITO anode but such a
layer may also serve as a hole injection enhancement layer.

20   The forward bias current-voltage (I-V) characteristics of 0.05
mm^2 IOLEDs with PTCDA and CuPc PCLs, which are shown in Fig. 2,
show that these characteristics are similar to previously
reported conventional IOLEDs, where trap limited conduction
was observed, Z. Shen et al., Jpn. J. Appl. Phys. 35, L401
25   (1996), P.E. Burrows J. Appl. Phys. 79, 7991 (1996), ($i \alpha$
$V^{(m+1)}$). For the IOLEDs, m = 8 independent of the details of
the particular device structure or PCL thickness. The EL
brightness at a current density of 10 mA/cm^2 was between 40 and
100 cd/m^2 for all devices, independent of details of the HTL,
30   PCL or anode structure. The IOLEDs, whose characteristics are
presented in Fig. 2, are a representative sample of devices
with different thicknesses of PTCDA or CuPc. The operating
voltage of IOLEDs employing CuPc as the PCL was independent of
CuPc thickness between 40 Å and 170 Å. In contrast, the
35   operating voltage of PTCDA-protected IOLEDs abruptly decreased
by 1.5 V as the PTCDA thickness increased from 40 Å to 60 Å.
The voltage drop across the PCL is typically small compared to

that across the rest of the device, since PTCDA and CuPc are
both thinner and more conductive. Therefore, the abrupt
change in the I-V characteristics reflects a change in the
hole injection efficiency from the ITO contact.

5

While not intending to be limited to the precise theory of how
the hole injection efficiency is enhanced for OLEDs containing
a PCL, the enhancement is believed to be partly due to the
reduced damage of the vacuum deposited hole transport layer
10   during deposition of the ITO layer and partly due to a reduced
barrier for hole injection from ITO into the hole injection
enhancement layer. The ITO sputter deposition typically
inflicts film damage to the top-most organic layer. This
damage results in only a 30% yield out of 15 devices with no
15   PCL, as compared to 100% yield for devices with either a PTCDA
or CuPc PCL. The abrupt increase in the operating voltage for
IOLEDs with < 40 Å thick PTCDA layers occurs when the
thickness of the damaged region is comparable to the PCL
thickness. At this point, further deposition of ITO degrades
20   the TPD which becomes directly exposed to the sputtering
plasma.

The presence of the PCL also influences the maximum drive
current before device breakdown (I_{max}), where I_{max} for an IOLED
25   with no PCL is only 10% of that obtained for IOLEDs with
either a PTCDA or CuPc PCL. The differences in I_{max} are
evident in both Figs. 2 and 3, where all IOLEDs were driven at
continuously higher currents until device breakdown occurred.

30   The PCL is, therefore, shown herein to protect the underlying
organic materials, to decrease the IOLED operating voltage,
and to increases I_{max} of the IOLEDs prepared containing the
PCL. A similar decrease in the operating voltage was
previously observed for conventional OLEDs with a CuPc coated
35   ITO anode, *S.A. VanSlyke et al., Appl. Phys. Lett 69, 2160
(1996)*. This is believed to be due to a reduced energy
barrier to hole injection from the ITO into CuPc as opposed to

the energy barrier between the ITO and the HTL. The lowest
transition voltage (i.e. the voltage at which ohmic conduction
and trap limited conduction are equal) was achieved for IOLEDs
with > 100 Å thick PTCDA PCLs. These results show an enhanced
5 hole injection efficiency as compared with IOLED devices not
including the PCL.

Fig. 3 shows the light intensity vs. current (L-I) response of
the IOLEDs in Fig. 2. The external EL quantum efficiency of
10 the protected IOLEDs was η = (0.15 ± 0.01)% vs. η = (0.30 ±
0.02)% for the unprotected devices. This difference is
believed to be due in part to absorption by the PCL, since
both CuPc and PTCDA exhibit a strong absorption at the peak
Alq_3 emission wavelength of 530 nm. For example, η decreases
15 by 25% as the CuPc PCL thickness increases from 40 Å to 170 Å.
Similarly, η for PTCDA-protected IOLEDs decreases by 25% with
an increase in PTCDA film thickness from 10 Å to 120 Å,
consistent with PTCDA absorption. The origin of the remaining
difference in η between IOLEDs with and without a PCL is not
20 understood, although it is believed that defects at the
PTCDA/ITO interface may scatter a fraction of the emitted
light back into the PTCDA where it can experience further
absorption. A different PCL material, some of which are
described above, which is transparent to Alq_3 emission is thus
25 expected to increase the IOLED efficiency somewhat. The shape
of the EL emission spectra of IOLEDs with PCLs is similar to
that of conventional Alq_3-based OLEDs (Fig. 4). The IOLED
spectrum with a 60 Å thick PTCDA PCL is slightly broadened due
to the PCL absorption.
30
The results shown in Fig. 5 show that a surface-emitting, or
inverted organic LED (IOLED) with a cathode as a bottom
contact and using a novel anode comprised of an organic hole-
injecting PCL and a transparent, sputter-deposited ITO thin
35 film could produce enhanced hole injection efficiency as
compared with IOLEDs lacking such a PCL. The IOLED can be
grown on top of any smooth substrate to which the cathode will

adhere, including opaque substrates such as Si and metal foils. The IOLED I-V characteristics and EL spectra were similar to that of conventional OLEDs, while the operating voltage is higher and efficiency somewhat decreased,

5 indicating the need for further optimization of the device contacts.

Still another aspect of the present invention is directed to an alternative method for reducing or preventing the ITO

10 sputtering damage. This method may be used in place of or in addition to using the protection layer. In this method, the ITO layer is deposited initially at a relatively low ITO deposition rate so as to avoid causing damage to the underlying organic layers and then the ITO layer is deposited

15 at a relatively high rate, so as to reduce the time required to fabricate the OLEDs. In particular, during the initial stages of the ITO deposition process, when substantial damage to the OLED surface may occur, the ITO deposition rate is preferably only about 2-5 Å/minute. However, after the

20 growing ITO layer reaches a certain threshold thickness that is sufficient to protect the underlying layer or layers, the deposition rate may be increased several fold, preferably, to a deposition rate that is at least 5 to 10 times higher than the initial deposition rate. Though the improved ITO

25 deposition method is preferably used in combination with a protection layer, the improved ITO deposition method may in some cases be used without using the protection layer.

For the RF power supply used to prepare the ITO layers

30 according to the subject method, which was an Advanced Energy ATX-600 RF power supply, Fort Collins, Colorado, USA, the power settings may be varied from about 1W-7W for the low ITO deposition rates and from about 20W-40W for the higher ITO deposition rates. Thus, in going from the low ITO deposition

35 rate up the higher ITO deposition rate, there may be an increase in the power settings of the RF power supply from as much as about a 3-fold increase up to about a 40-fold

increase. Preferably, the increase is such as to produce an increase in the ITO deposition rate of at least from about a 5-fold increase up to about a 10-fold increase.

5   The underlying layer or layers may be a thin and relatively fragile Mg:Ag cathode layer, an organic layer that is under the Mg:Ag cathode layer, and/or an organic layer, such as a hole transporting layer, onto which the ITO layer is directly deposited, for example, whenever an IOLED is being fabricated.
10   As described herein, a low ITO deposition rate is one for which no practically discernible damage to a fragile layer can be detected and a high ITO deposition rate is one for which discernible damage to a fragile layer can be detected.

15   A threshold thickness of ITO that is sufficient to protect the underlying layer or layers from damage during the ITO deposition process, herein referred to as a "protective ITO layer," is one for which no practically discernible difference is observed in the I-V characteristics for OLEDs prepared
20   using the higher ITO deposition rates, as compared with OLEDs wherein the ITO layer is prepared using only the low, non-damaging, ITO deposition rates. No practically discernible difference in I-V characteristics is one for which, over the range of voltages applied across a particular OLED structure,
25   the voltage required to obtain a particular current is within about 20% of the value that can be observed for that particular OLED structure whenever the ITO is deposited only at the low, non-damaging, ITO deposition rates.

30   While the threshold thickness of the growing layer of ITO that is required to protect the underlying layers may vary depending on the actual materials that are in the underlying layers, this threshold thickness is preferably about 50 to 200 Å, and more preferably about 50 to 100 Å, before substantially
35   increasing the deposition rate. While the maximum rate that may be used without causing damage may also vary over a substantial range, also depending on the actual materials

being coated, the deposition rate may be increased from about
2-5 Å/minute to at least about 50 to about 60 Å per minute.
Programming the deposition process so as to gradually and
continuously increase the ITO deposition rate throughout the
5   process or, alternatively, to continuously increase the ITO
deposition rate only after a certain threshold ITO thickness
is reached also falls fully within the scope and spirit of the
present invention. In such cases, whenever the ITO deposition
rate is increased gradually and continuously, it is to be
10   understood that the threshold thickness that is sufficient to
function as the protective ITO layer may be somewhat thinner
than that required whenever the ITO deposition rate is
abruptly increased to a substantially higher ITO deposition
rate.
15
The performance of the OLEDs prepared using the present
invention may be evaluated by comparing the I-V
characteristics of OLEDs made using the accelerated ITO
deposition rate as compared with OLEDs prepared using a single
20   ITO deposition rate throughout the ITO deposition process. It
was discovered that OLEDs prepared using the present
accelerated deposition rate method could be made with I-V
characteristics having no practically discernible difference
from the I-V characteristics of an OLED in which the
25   deposition rate was kept at a low deposition rate throughout
the ITO deposition process.

In the preferred embodiments of the present invention, the ITO
layer is sputtered using an RF power source onto the target in
30   the presence of an oxygen flux that is selected to provide the
desired combination of transparency and electrical resistivity
values for a given ITO layer thickness. The actual oxygen
flux that is selected may vary widely depending on the
characteristics of the specific fabrication system used and
35   may be evaluated in terms of the absorption of visible
radiation by the ITO layer. In particular, it is preferable
that the absorption of visible radiation, which varies as a

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function of wavelength over the visible region of the
spectrum, be such as to produce a total light transmission,
for the ITO layers made using the accelerated deposition
rates, comparable to that for ITO coatings prepared at the
5   lower ITO deposition rates.

The oxygen flux may vary over the range from about 0.35 to
about 0.50 sccm ("standard cm^3/minute") for the higher ITO
deposition rates and from none at all up to about 0.2 sccm,
10   preferably, about 0.1 sccm, for the much lower ITO deposition
rates. Using these criteria to evaluate the performance of
the ITO layers prepared using the subject method, it has been
found that an increase in the ITO deposition rate of at least
ten-fold could be used to produce ITO coatings having I-V
15   characteristics nearly identical to coatings prepared using
only the lowest ITO deposition rates. Such an increase is
typically produced by using a ten-fold increase in the RF
power settings.

20   In a further aspect of the present invention, the electron
transporting layer of OLEDs made according to the present
invention may be comprised of an organic free radical, which
may be prepared in a manner that is suitable for fabricating
the electron transport layer of an OLED. In a representative
25   embodiment of the present invention, the electron transporting
material is represented by the chemical structure, $Cp^{Ar\cdot}$, of
formula (I):

(I)

30   which is herein referred to as multi-aryl-substituted
cyclopentadienyl free radical, wherein each Ar-group, Ar_1, Ar_2,

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Ar_3, Ar_4 and Ar_5, is hydrogen, an alkyl group or an unsubstituted or substituted aromatic group. Although the term "Ar-group" may typically be used to refer only to aryl groups, the term is used herein to include hydrogen or an
5 alkyl group even though, preferably, at most only one of the Ar-groups is an alkyl group or hydrogen, with the remainder being aromatic groups, and, most preferably, all of the Ar-groups being aromatic groups. The aromatic groups may be independently selected to be the same or different, one from
10 the other, with the total number of compounds that may be embraced by formula I being limited only insofar as they may be suitable for use in preparing an electron transporting layer and insofar as it is chemically practical to prepare such compounds. An organic free radical compound is herein
15 defined to be suitable for use as an electron transporting material if the carrier mobility of the electron transporting layer has a value of at least 10^{-6} cm^2/V sec.

The unsubstituted or substituted aromatic groups may be, for
20 example, phenyl groups; groups having fused phenyl rings, such as naphthyl; or aromatic heterocyclic groups such as pyridyl or thiophenyl.

Each aromatic group may be, independently of the other
25 aromatic groups, unsubstituted or substituted with one or more substituent groups. The substituent group, or groups, may be an electron donor group, an electron acceptor group or an alkyl group.
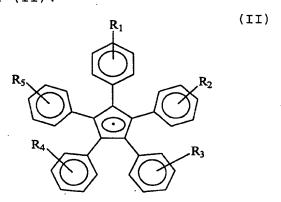
30 For those compounds which function not only as an election transporting material but also serve as an emissive material, the unsubstituted or substituted aromatic group may be selected so as to adjust the spectral emission characteristics in a manner such as to produce a desired color, as
35 characterized, for example, by using the X-Y chromaticity coordinates of the CIE colorimetric system. For example, it is known that substantial changes in the emission spectra of a

phenyl-containing compound may be produced dependent on whether the phenyl group is unsubstituted or is instead substituted in the ortho or para position with an electron donor group or an electron acceptor group. In addition to
5 being selected to adjust the emission characteristics, the donor and acceptor groups may also be selected to affect the degree of intermolecular interaction and, thus, carrier mobility. Moreover, such substituents may also be selected so as to adjust the reduction potential of the organic free
10 radicals, that is, the energy required to reduce the free radicals, thus converting the free radicals to the anions of the free radical. By suitably selecting the substituents to produce a readily accessible reduction potential, the carrier mobility and/or the carrier trap depth may be favorably
15 altered, such that stable organic free radicals may be produced that have an overall combination of electron-transporting and electron-emissive properties that is particularly suitable for use as an electron transporting layer.
20

Still more specifically, in a preferred embodiment, the organic free radical is a pentaphenylcyclopentadienyl radical, Cp$^{\Phi}$· of formula (II):

(II)

wherein each aryl group of formula (I) is defined in formula
(II) as being a single phenyl group that may be unsubstituted,
or substituted with the substituents R_1, R_2, R_3, R_4 and R_5,
respectively, wherein each R-group represents independently
5   from the other R-groups, one or more of an electron donor
group, an electron acceptor group or an alkyl group.

As a specific illustrative embodiment of the present
invention, the organic free radical may be the unsubstituted
10 $Cp^{\Phi}\cdot$, as represented by formula (III):

(III)

As still another specific illustrative embodiment of the
present invention, the organic free radical may be the
15 tetraphenylcyclopentadienyl free radical of formula (IV),

(IV)

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and further-substituted variations thereof, for example,
wherein the hydrogen shown in formula (IV) may be replaced by
an alkyl group.

5   While not intending to be limited by the theory of the
     invention for the representative embodiments of the specific
     organic free radicals as disclosed herein, it is believed that
     the effectiveness of the $Cp^{Ar \cdot}$ free radical as an electron
     transporting material in the ETL of an OLED may be based on a
10   combination of properties. These include the presence of a
     sterically shielded central cyclopentadienyl ring, which can
     form an unusually stable organic free radical because of the
     substantially complete steric shielding of the
     cyclopentadienyl ring; the ability of the cyclopentadienyl
15   free radical to readily form an anion, which acting together
     with the free radical, serves as an electron carrier; and the
     strong aromatic character of the cyclopentadienyl anion, which
     results in strong overlap of the Π-orbitals of the anion with
     the Π-orbitals of the phenyl substituents, thus enhancing the
20   election mobility that promotes effectiveness of the material
     as an electron carrier. The present invention has the further
     feature that the substituents that are included in the organic
     free radicals may be selected so as to alter the emissive
     spectra and the reduction potential of the free radical in a
25   manner so as to produce an overall combination of electron-
     transporting and electron-emissive properties that is
     particularly suitable for use as an electron transporting
     layer.

30   The present invention is thus directed to electron
     transporting materials suitable for use in the electron
     transporting layer of an OLED, wherein the electron
     transporting material is comprised of a stable organic free
     radical having a readily accessible reduction potential
35   between the stable organic free radical and the anion formed
     from the radical, for example, the pentaphenylcyclopentadienyl

free radical, Cp$^\varnothing$·, of formula (III) and the
pentaphenylcyclopentadienyl anion of formula (V):

— (V)

5   A ready accessible reduction potential leads to suitable
    electron conduction through the electron transporting layer,
    wherein suitable electron conduction is herein defined to mean
    an electron conduction based on having an electron mobility of
    at least about 10^{-6} cm^2/V sec.

10

    An electron transporting layer comprised of the Cp$^\varPhi$· free
    radical provides a further advantage in that the electron
    transporting material may, in some cases, also function as an
    emissive material in the OLED. Whenever the electron

15 transporting material also serves as an emissive material, the
    OLED may be fabricated using a single heterostructure. If the
    electron transporting material does not also serve as an
    emissive material, the OLED may be fabricated from a single
    heterostructure in which the hole transporting layer is the

20 emissive layer or from a double heterostructure.

    The present invention is further directed toward a novel
    method for preparing the Cp$^\varPhi$· free radical in bulk form as a
    thin layer of electron transporting material having a high

25 electron mobility and a high electron carrier density, wherein
    the electron transporting layer is included in a multi-layer

structure, in particular, a heterostructure for producing
electroluminescence. It is believed that no prior art
electron transporting materials have been disclosed which are
comprised of an organic free radical. Thus, while the present
5 invention is directed toward use of a multi-aryl-substituted
cyclopentadienyl free radical, or more specifically, a multi-
phenyl-substituted cyclopentadienyl free radical, or still
more specifically, a pentaphenylcyclopentadienyl free radical
as a species representing the preferred embodiment, it is to
10 be understood that the present invention is generally directed
toward any organic free radical that may be contained in an
electron transporting layer as an electron transporting
material having an electron mobility of at least 10^{-6} cm^2/V
sec.

15

In addition to being a free radical, the Cp^{Φ}· free radical
differs from the pentaphenylcyclopentadiene itself, $Cp^{\Phi}H$:

20

in that $Cp^{\Phi}H$ has been reported to be a blue emitting material
when used in OLEDs, C. Adachi et al., Appl. Phys. Lett., vol.
56, 799-801 (1990), whereas a film of the
25 pentaphenylcyclopentadienyl free radical has been observed and
reported to have a purple color, M.J. Heeg et al., J.
Organometallic Chem., vol. 346, 321-332 (1988).

Furthermore, the Cp^{Φ}· free radical differs from $Cp^{\Phi}H$ in that the
30 latter is not readily reduced. Reduction of $Cp^{\Phi}H$ would have to
be followed by loss of H^+ to give the stable anionic form,
which is not energetically feasible. In particular, whereas

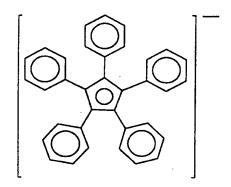there is no reason to expect, based on these differences, that $Cp^\Phi H$ would have good carrier transport properties at all, the $Cp^{\Phi\cdot}$ free radical is capable of being especially well suited for this purpose.

Another feature of the present invention is based on the fact that, while it is typically difficult to prepare and store $Cp^{\Phi\cdot}$ by conventional methods, the $Cp^{\Phi\cdot}$ free radical material of the present invention may be readily prepared *in vacuo* from air-stable precursor complexes. The metallocene complexes of pentaphenylcyclopentadiene, such as $(Cp^\Phi)_2M$, where M = Fe, Ru, Sn, Ge or Pb, may be prepared as disclosed in *Heeg et al*. These materials can be prepared from the metal salts and the Cp^Φ anion, $[Cp^\Phi]^-$,

as illustrated by the following equation:

$$MX_2 + 2\ Cp^\Phi Li \rightarrow (Cp^\Phi)_2M + 2LiX,\quad (1)$$

where M = Fe, Ru, Sn, Ge or Pb; and X = halide or acetate. Each of these complexes are air stable complexes. However, the Ge and Pb complexes are not thermally stable. Attempted sublimation of the Ge and Pb complexes at 250°C and about 10^{-4} torr was reported to lead to formation of a metal mirror and sublimation of the gaseous $Cp^{\Phi\cdot}$ free radical species, as shown by the following equation:

$$(Cp^{\oplus})_2M' \quad \xrightarrow[\substack{250°C \\ 10^{-4} \text{ torr}}]{} \quad M'(\text{solid}) + 2\ Cp^{\oplus\cdot} \quad (\text{gas phase}) \qquad (2)$$

5   The purple films which are deposited from the gas phase
organic free radical, $Cp^{\oplus\cdot}$, are comprised only of the $Cp^{\oplus\cdot}$ free
radical material, according to Heeg et al.

The present invention is directed toward using such precursor
10   materials and such methods to prepare electron transporting
layers that may be used in substantially any type of multi-
layer structure that includes an electron transporting layer.
In particular, the free-radical-containing, electron
transporting layer may be included, for example, in the multi-
15   layer structure of a light emitting device, that is, in a
heterostructure for producing electroluminescence. The
present invention is, thus, directed to incorporating the
subject electron transporting layers into multi-layer
structures wherein the electron transporting layer is in
20   electrical contact with a hole transporting layer.

The stable organic free-radical-containing materials are
intended to provide benefits and advantages that are uniquely
suited for use as an electron transporting material, when such
25   free-radical-containing materials are incorporated into a
multi-layer structure as the electron transporting layer.
While it is intended, in the more preferred embodiments of the
present invention, that the electron transporting layer be
comprised predominantly of an organic free radical, or even,
30   in some cases, be directed to electron transporting layers
consisting essentially of organic free radicals, it is also
contemplated that layers containing free radical materials
that have undergone dimerization, even substantial
dimerization, may also serve as effective electron
35   transporting materials, and are, therefore, also contemplated
to fall within the scope of the present invention.

In fact, while the electron transporting layer be comprised

predominantly, if not completely, of an organic free radical
material, the present invention may embrace any electron
transporting layer that includes an organic free radical
material for which it can be shown that the presence of the
5   organic free radical contributes to the electron-transporting
characteristics of the electron transporting layer. For
example, the layer may be comprised of organic free radical
materials that are embedded in a matrix of non-free-radical,
but still electron-transporting, material. An electron
10   transporting layer comprised predominantly of an organic free
radical is herein defined as a layer in which the organic free
radical is the major component of the electron transporting
layer.

15   In the preferred embodiments of the present invention, the Ge
(decaphenylgermanocene) or Pb (decaphenyl-plumbocene) complex
of pentaphenylcyclopentadienyl is used as the source for
preparing the thin layers of $Cp^{\Phi \cdot}$ in a vacuum deposition
system.
20

The present invention is further directed to OLEDs in which
dopant compounds may be included in the emissive layer. A
dopant capable of shifting the emission wavelength of an
emissive layer comprised only of a host compound is added to
25   the host compound in an amount effective to shift the
wavelength of emission so that the LED device preferably emits
light that is perceived by the human eye to be close to one of
the primary colors. Although it is recognized that
characterization of color perception is a subjective exercise,
30   a quantitative chromaticity scale has been developed by the
Commission Internationale de l'Eclairage (International
Commission of Illumination), otherwise known as the CIE
standard. According to this standard, a saturated color may
be represented by a single point, with specific quantitative
35   coordinates according to the defined axes of the chromaticity
scale. It will be appreciated by one of skill in the art that
such a single point on the CIE scale would represent a

standard or a goal that, in practical terms, is difficult, but
fortunately, unnecessary, to attain.

5   In the preferred embodiments of the present invention in which
the OLED produces a primary color, the dopant is incorporated
into a host compound so that the OLED emits light that is
perceived by the human eye to be close to a saturated primary
color. Through the practice of the present invention, it is
intended that OLEDs be constructed which can be characterized
10   by an emission that is close to an absolute (or saturated)
chromaticity value, as that would be defined by the CIE scale.
Furthermore, LED's utilizing the materials of the present
invention are also intended to be capable of a display
brightness that can be in excess of 100 cd/m^2 although somewhat
15   lower values, perhaps as low as 10 cd/m^2, may be acceptable in
certain cases.

The host compounds as defined herein are compounds which can
be doped with dopants to emit light with the desired spectral
20   characteristics. The term "host" is used to refer to the
compound in the emissive layer that functions as the component
which receives the hole/electron recombination energy and then
by an emission/absorption energy transfer process, transfers
that excitation energy to the dopant compound, which is
25   typically present in much lower concentrations. The dopant
may then relax to an excited state having a slightly lower
energy level, which preferentially radiates all of its energy
as luminescent emission in a desired spectral region. A
dopant that radiates 100% of the dopant's excited state
30   excitation energy is said to have a quantum efficiency of
100%. For host/dopant concentrations which are to be used in
a color tunable SOLED, preferably most, if not all, of the
host's excitation energy is transferred to the dopant which in
turn radiates, perhaps from a lower energy level, but with a
35   high quantum efficiency, to produce visible radiation having a
desired chromaticity.

As the term host compound is used herein, it will be
appreciated that such compounds can be found in either an
electron transporting/emissive layer of a single
heterostructure OLED device or in the separate emissive layer

5   of a double heterostructure device. As will be recognized by
one of skill in the art, use of the dopant species such as
disclosed herein makes it possible to extend not only the
range of colors emitted by the OLED, but also to extend the
range of possible candidate species for host and/or dopant

10 compounds. Accordingly, for effective host/dopant systems,
although the host compound can have a strong emission in a
region of the spectrum where the dopant species strongly
absorbs light, the host species preferably does not have an
emission band in a region where the dopant also emits

15 strongly. In structures where the host compound also
functions as a charge carrier, then additional criteria such
as redox potential for the species also becomes a
consideration. In general, however, the spectral
characteristics of the host and dopant species are the most

20 important criteria.

The amount of dopant that is present is that amount which is
sufficient to shift the emission wavelength of the host
material as close as possible to a saturated primary color, as

25 that would be defined according to the CIE scale. Typically,
the effective amount is from about 0.01 to 10.0 mol %, based
on the emitting layer. The preferred amount is from about 0.1
to 1.0 mol %. The primary criterion for determining an
appropriate doping level is the level which is effective for

30 achieving an emission with the appropriate spectral
characteristics. By way of example, and without limitation,
if the amount of dopant species is at too low a level, then
emission from the device will also comprise a component of
light from the host compound itself, which will be at shorter

35 wavelengths than the desired emission form the dopant species.
In contrast, if the level of dopant is too high, emission
efficiencies could be adversely affected by self-quenching, a

net non-emissive mechanism. Alternatively, too high levels of
the dopant species could also adversely affect the hole or
electron transporting properties of the host material.

5   A further embodiment of the present invention is directed, in
particular, to an emissive layer containing a host material of
a metal complex of (5-hydroxy)quinoxaline,

(V)

10 wherein M is Al, Ga, In, Zn or Mg, with n = 3, if M is Al, Ga
or In and n = 2, if M is Zn or Mg.

A still further embodiment of the present invention is
directed to dopant materials comprised of an inner salt having
15 the chemical structure of formula VI:

(VI)

wherein R_1, R_2, R_3 and R_4 are, independently of each other, an
unsubstituted or substituted alkyl, aryl or heterocycle (for
20 example, a pyrole), and R_5 and R_6 are, independently of each
other, an unsubstituted or substituted alkyl, aryl, OH or NH_2.
Such compounds are herein referred to as bisphenyl-squarilium
compounds.

Still more specifically, one of the embodiments of the present invention is directed to dopant materials comprised of an inner salt of a compound having the chemical structure of formula VII:

5

(VII)

$$R_2N \xrightarrow{\quad} \underset{\text{OH}}{\overset{\text{O}_-}{\bigcirc}} \overset{(2+)}{\square} \overset{\text{O}_-}{\underset{\text{HO}}{\bigcirc}} \xrightarrow{\quad} NR_2$$

wherein R = an alkyl. Such compounds are herein referred to as squarilium dyes.

10   Another embodiment of the present invention is directed to dopant materials comprised of an indigo dye compound having the chemical structure of formula VIII:

(VIII)

$$R_8 \xrightarrow{\quad} \underset{X}{\overset{O}{\bigcirc}} = \underset{O}{\overset{X}{\bigcirc}} \xrightarrow{\quad} R_7$$

15   wherein X = NH, NR$_9$, S, Se, Te, or O, wherein R$_9$ is alkyl or phenyl, and R$_7$ and R$_8$ are, independently of each other, an unsubstituted or substituted alkyl or aryl group, or a π-electron donor group such as -OR, -Br, -NR$_2$, etc. or a π-electron acceptor group such as -CN, -NO$_2$, etc.

20
Still more specifically, another of the embodiments of the present invention is directed to dopant materials comprised of an indigo dye compound having the chemical structure of formula IX:

25

(IX)

wherein X = NH.

Still another embodiment of the present invention is directed
to dopant materials comprised of a fullerene compound, for
example, the C_{60} fullerene compound.

As an illustrative example of the present invention, the host
compound, is preferably comprised of the compound of formula V
wherein M = Al and n = 3 aluminum tris(5-hydroxy-quinoxaline),
("Alx$_3$"):

(X)

and the dopant compound is preferably comprised of the
squarilium dye compound of formula XI, 1,3-bis[4-
(dimethylamino)-2-hydroxyphenyl]-2,4-
dihydroxycyclobuteneolyllum dihydroxide,bis(inner salt) [63842-
83-1]:

(XI)

- 40 -

Vacuum-deposited, single heterostructural OLEDs may be made
having an electron transporting layer comprised of a host
compound of formula X and a dopant compound of formula XI,
wherein the OLED has current-voltage (I-V) characteristics,
5   UV-visible, photoluminescence and electroluminescence
properties that are particularly suitable for OLEDs. It is
believed that the effectiveness of this particular host/dopant
combination is based on achieving a high level of energy
transfer from the host to the dopant. Such a high level of
10   energy transfer, for suitably matched hosts and dopants, can
lead to more efficient electroluminescence as compared to when
the host compound is used alone.

While not intending to be limited by the theory of the
15   invention for the representative embodiments as disclosed
herein, as a means of illustrating how such combinations of
host and dopant compounds can be selected and matched to
provide efficient electroluminescence (EL), the
photoluminescence (PL) of the host Alx_3 compound, with and
20   without the dopant dye compound, may be compared with Alq_3:

which was also prepared with and without the dopant compound.

The PL of these compounds may be measured using standard
25   techniques, for example, by immersing the compounds in a

solvent, exposing them to a photoexcitation source and
measuring the photoluminescence spectrum as a function of
wavelength using equipment such as is available from Photon
Technology International, in Somerville, New Jersey, USA.

5

The PL spectrum of Alq_3, Alx_3 and Gax_3 is shown in Fig. 11.
The Alx_3 produces an orange photoluminescence with a maximum at
about 620 nm, which is significantly red shifted relative to
Alq_3, which has a PL maximum at about 515 nm. It is believed

10   that this large red shift can be significant in helping to
achieve the high level of energy transfer from the host Alx_3
compound to the red fluorescent dye dopant. The EL spectra of
OLEDs prepared with an un-doped and doped Alx_3 layer are shown
in Fig. 12. Whereas the undoped host material has an EL

15   spectrum that is slightly red shifted as compared with the PL
spectrum of the host material, the maximum occurs in a
wavelength region that still has an orange appearance, as
characterized, for example, by the standard CIE colorimetric
system (x = 0.565, y = 0.426). However, when this host

20   material is doped with the inner salt dye of formula XI, the
EL spectrum has a maximum in a wavelength region that is
significantly shifted toward the red (x = 0.561, y = 0.403).

Further embodiments of the present invention are directed to
25   OLEDs having an emissive layer containing a dopant comprised
of an indigo dye compound of formula VIII or of a fullerene
compound. Without in any way limiting the scope of these
classes of compounds, species of these classes of compounds
are represented by the indigo dye compound of formula IX and
30   the fullerene compound C_{60}. The absorbance spectra of these
compounds, as shown in Fig. 14, together with the bisphenol
squarilium compound of formula XI, show that these compounds
have absorption bandwidths which are suitably matched to
accept the photoluminescence from the host compounds Alx_3 and
35   Alq_3.

The photoluminescent spectra of these dopants, as shown in
Fig. 15, show that each of these compounds produces
luminescence in or toward the red region of the visible
spectrum. Furthermore, as illustrated by the
5 electroluminescent spectra of OLEDs incorporating the
fullerene or squarilium dye dopants in a single
heterostructural device using Alx_3 or Alq_3 as the host
material, each of these compounds is shown to be capable, at
sufficient dopant concentrations, of having the excitation
10 energy completely transferred from the host, see Figs. 16, 17,
18. Part of that energy is then radiated as
electroluminescence by the dopant. The capacity for a dopant
to replace substantially all of the emission of the host
compound with that of the dopant is of particular benefit, for
15 example, in a color tunable SOLED. In such devices, which
have more than one color-emitting layer, it is desirable to
have each layer with its own well-defined chromaticity and
with a spectral emission that does not overlap the spectral
emission of any other layer.
20

The electroluminescent emission of an OLED containing the
representative indigo dye compound is shown to have an
emission band having a maximum near 650 nm (with CIE values,
x=0.693 and y=0.305), which produces a saturated red
25 appearance.

The Zn and Mg derivatives of (5-hydroxy)quinoxaline have also
been prepared and found to produce PL spectra nearly identical
to that observed for Alx_3. In view of the effectiveness of
30 Alx_3 as a host material for red-emitting dopants wherein there
is also a good energy match, such PL spectra show that the Zn
and Mg derivatives may also be useful as host materials for
suitably selected red-emitting dopants.

35 The Ga derivative of (5-hydroxy)quinoxaline has also been
prepared and found to have the PL emission spectrum as shown
in Fig. 11. These results show that the Ga analog may be

effective not only as a doped emissive material, but also as
an un-doped material.

Examples of additional host or receiving compounds include
5   emitting compounds and/or host compounds of the type shown and
described in Applicants' co-pending U.S. Patent Application
Serial No. 08/693,359, filed 6 August 1996. Further
representative examples of the present invention include
emitting compounds according to Formula XII:
10

(XII)

wherein M is a trivalent metal ion of a metal such as Al or
Ga; and R is alkyl, phenyl, substituted alkyl, substituted
15   phenyl, trimethylsilyl, or substituted trimethylsilyl; and
wherein X, Y, and Z are each individually and independently C
or N, such that at least two of X, Y and Z are N; and of
Formula XIII:

20   (XIII)

Specific examples of compounds according to Formula I are
provided in Fig. 20, which are all commercially available
species (Aldrich Chemical Co., Inc.).

5   A frequently used emitting compound utilized in those green-
emitting OLED's, as disclosed in a number of United States
Patents assigned to Kodak (see, for example U.S. Patent No.
5,552,678 to Tang et al.), is a quinolate complex of the
general formula:

10

wherein M is a trivalent ion of metals such as aluminum and
gallium. An exemplary green-emitting compound according to
this general formula would be tris(8-hydroxyquinolato)
15   aluminum, also referred to as Alq_3. Compounds of the present
invention as represented by formulas XII and XIII have a red-
shifted emission due to the altered ligand structure. The
selection of the compounds of formula XII is based on the
observation that the incorporation of two nitrogen heteroatoms
20   into the pyridil side of the quinolate ligand results in a
shift of emission wavelength of 100 nm relative to the
emission from Alq_3.

Using this approach for red-shifting the emission of an OLED,
25   the compounds of Formulas XII have been devised and
synthesized with the specific purpose of shifting the emission
from Alq_3-type receiving compound materials toward shorter

wavelengths. The ligand of Formula XII is an example of a
fused ring, multi-heteroatom structure that offers many of the
same structural features of the quinolate-based ligands, yet
has an emission shifted considerably from that of Alq_3.

5

The compound represented by Formula XIII, although not a metal
complex, may be prepared as the hole conducting material for
an HTL layer in an OLED. In addition to functioning as the
hole transporting material the compound of formula XIII also
10 exhibits satisfactory emissive characteristics as well. The
emissive properties of this compound, as well as a compound of
Formula XII, are summarized below. Also provided are
comparable data for the Alq_3 compound.

15

TABLE 1		
Compound	absorption λ	emission λ
Alq_3	380 nm	540 nm
XII	280 nm	390 nm
XIII	355 nm	402 nm

20
In accordance with another embodiment of the present
invention, Fig. 22 shows a high contrast TOLED display under
bright ambient light conditions, such as in sunlight. The
high contrast TOLED display of the present invention comprises
25 a TOLED display TD and a low-reflectance absorber, such as a
black absorber BA arranged behind the display TD. The TOLED
display TD can be fabricated as disclosed in U.S. Patent
Applications Serial Nos. 08/354,674 and 08/613,207,
incorporated herein by reference in their entirety.

30

As illustrated in Fig. 22, light R emitted from a bright light
source L, such as the sun, passes through the various layers
of the TOLED display TD and is absorbed by the black absorber
BA. As a result, light I emitted by the display TD and viewed
35 by a viewer V is not washed out by ambient light which is

reflected by the display, as is the case with conventional displays.

A cross-sectional view of an embodiment of a high contrast
5   display in accordance with the present invention is shown in
    Fig. 23. A TOLED 1 is arranged over a transparent substrate 2
    which is arranged over a low-reflectance absorber 3. Light I
    emitted from the TOLED 1 propagates toward the viewer. The
    TOLED 1, which is comprised of several different layers of
10 materials is shown, for simplicity, as one layer. The
    transparent substrate 2 can be comprised of glass or of
    plastic, which may be flexible or rigid.

    The low-reflectance absorber 3 can be comprised, for example,
15 of a layer of paper or cardboard painted or printed black at
    least on the side facing the substrate 2. The low-reflectance
    absorber 3 can also be deposited directly onto the bottom side
    of the substrate 2, such as by painting the bottom of the
    substrate with a black, preferably matte, paint. The low-
20 reflectance absorber 3 can also be implemented by spin coating
    carbon black onto a polymer matrix or by evaporation
    deposition.

    A cross-sectional view of a second embodiment of a high
25 contrast display in accordance with the present invention is
    shown in Fig. 24. In this embodiment, a low-reflectance
    absorber 3 is arranged between a TOLED 1 and a substrate 2.
    In the embodiment of Fig. 24, the low-reflectance absorber 3
    is deposited onto the substrate 2. The substrate 2 need not
30 be transparent. The low-reflectance absorber 3 and the
    substrate 2 can also be implemented as one layer.

    Because it is desirable to make the surface of the low-
    reflectance absorber 3 facing the viewer as absorptive as
35 possible, this surface may be relatively rough and thus may be
    undesirable for the fabrication thereon of the TOLED 1. As
    such, if need be, a planarizing layer 4 can be deposited on

the reflectance absorber 3 to provide a smooth surface on
which to deposit the TOLED 1. The planarizing layer 4 can be
comprised, for instance, of a polymer or plastic and can be
applied by spin coating.

5

While the low-reflectance absorber can be implemented, as
described above, as a "black absorber," the present invention
may also embrace the use of a low-reflectance absorber having
a color different from that of the color emitted by the TOLED.
10   For example, a dark green absorber behind a red-emitting
TOLED, or still other combinations of selected colors, may
also be used within the scope of the subject invention so as
to provide a high color contrast display. The low-reflectance
surface, thus, may have a high light absorption across the
15   entire visible region of the spectrum so as to produce a gray-
to-black surface or it may have high absorption only over that
part of the spectral region corresponding to the wavelength
region generated by the light emitting device. Preferably,
the absorption of light is at least about 50%, and more
20   preferably, about 80-90%, or still higher, for a black
absorber.

In order to extract even more EL light in the direction normal
to the OLED, an antireflection (AR) coating can be deposited
25   on the transparent ITO anode. For a conventional OLED, this
entails depositing the AR coating on top of the transparent
substrate prior to the deposition of the ITO layer and the
rest of the OLED layers. In such a configuration, care must
be taken to account for the reflections in the transparent
30   substrate. For an IOLED, the EL light does not travel through
the substrate, simplifying the AR coating design. Also, with
the IOLED, the AR coating can be deposited directly on the
anode and thus can at the same time serve as a passivating
layer for protecting the IOLED from atmosphere-related
35   degradation.

The IOLED structure of the present invention can also be
fabricated with one or more filter structures for controlling
the spectral width of the light emitted. Fig. 29 shows an
IOLED 50 fabricated over a distributed Bragg reflector (DBR)
5   structure 60 which is fabricated on a substrate 70. A DBR
structure may also be referred to as a multilayer stack (MLS),
such as taught by *H. A. MacLeod, Thin Film Optical Filters 94-
110 (1969).* The DBR structure 60 is formed as a 1/4-
wavelength stack 62 of highly reflective layers of dielectric
10   material. The stack 62 can be formed with two to ten
alternating layers of titanium oxide TiO_2 and silicon oxide
SiO_2. A layer 61 of ITO is deposited on the stack 62. The
cathode 55 of the OLED 50, which is formed as a thin, semi-
transparent layer of Mg:Ag alloy, is deposited on the ITO
15   layer 61. The ETL/EL layer 54, HTL 53, protection layer 52
and ITO anode 51 are then deposited in sequence.

The combination of the ITO anode 51 and the bottom DBR
structure 60 can provide good cavity and microcavity effect.
20   In particular, if the thickness of the ETL/EL layer 54 is
substantially equal to $\lambda/2n$, where λ is the wavelength of the
emitted light and n is the refractive index of the ITO anode
layer 51 (which is approximately 2.0, relative to air),
spectral narrowing is achieved with a considerable increase in
25   the effective efficiency of the OLED.

To narrow the spectrum of the light emitted by the OLED of
Fig. 29 even further, another DBR structure can be placed on
top of the OLED 50. This, however, requires that electrical
30   access to the anode 51 of the OLED be provided from a side of
the combined structure. As an alternative, such a top-side
DBR can be replaced by a color filter layer consisting of, for
example, an organic dye film.

35   The present invention further provides monochromatic and
multicolor light emitting devices that make use of phosphor
layers to downconvert the color of light emitted from organic

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light emitting materials into different colors. In one
embodiment of the invention, a downconversion layer is used to
convert blue light emitted from an organic light emitting
layer into red light within a stacked arrangement of OLEDs.
5 In another embodiment of the invention, downconversion layers
are used to convert blue light emitted from organic light
emitting layers into green and/or red light. The light
emitting devices of the present invention are used in a
variety of monochromatic and multicolor applications to
10 provide displays with high brightnesses and efficiencies.

The present invention may also provide organic light emitting
devices which make use of downconversion phosphor layers to
provide displays of high efficiency and brightness. A light
15 emitting device in accordance with the present invention
comprises a plurality of organic light emitting layers in a
stacked arrangement and a downconversion phosphor layer
disposed between any two of the plurality of organic light
emitting layers.
20
In a first embodiment of the present invention that relates to
downconversion phosphors, a light emitting device 100 is
provided as shown in Fig. 25. In this stacked arrangement of
organic light emitting layers, a first blue light emitting
25 layer 112 is provided over substrate 111, green light emitting
layer 113 is provided over first blue light emitting layer
112, red downconversion phosphor layer 114 is provided over
green light emitting layer 113, and second blue light emitting
layer 115 is provided over downconversion phosphor layer 114.
30 Disposed between the light emitting layers are transparent,
conductive layers 120, 121, 122 and 123. Metal contact layer
130 is provided over second blue light emitting layer 115.

Disposed between green light emitting layer 113 and red
35 downconversion phosphor layer 114 is a mirror structure 125,
which is preferably a multilayer stack of dielectric material.
Mirror structure 125 shown in Fig. 25 is characterized by a

red pass-band and blue and green blocking bands to prevent the
pumping of red downconversion phosphor layer 114 by green and
blue light emitting layers, 113 and 112, respectively. By
reflecting green and blue light, mirror structure 125 also
5   serves to increase device efficiency by a factor of at least
two. Moreover, mirror structure 125 results in the efficient
pumping of red downconversion phosphor layer 114 by second
blue light emitting layer 115 such that layer 114 is much less
thick than is necessary for a single-pass device. For
10   example, red downconversion phosphor layer 114 is as thin as
1000 Å.

Mirror structure 125 is any suitable material to permit the
passage of red light but block the passage of green and blue
15   light, as is known in the art. For example, mirror structure
125 comprises at least two dielectric materials with different
dielectric constants arranged in a multilayer stack. The
thickness of the layers in the stack define the range of
wavelengths that are permitted to pass through the structure.
20   Typical inorganic dielectric materials to form mirror
structure 125 include SiO_2/TiO_2 and SiO_2/SiN_x. Although such
inorganic materials are within the scope of the present
invention, the use of organic dielectric materials such as 3,
5, 7, 8 naphthalene tetracarboxylic dianhydride ("NTCDA") and
25   polytetrafluorethylene (TEFLON) are preferred. The use of
organic dielectric materials minimizes the risk of damaging
the organic light emitting materials during deposition of the
dielectric materials used for mirror structure 125.

30   As is known in the art, light emitting layers 112, 113 and 115
are made from organic materials that emit light when excited
by electric current. Therefore, the light emitting device
shown in Fig. 25 will emit blue light when a voltage is
applied across conductive layers 120 and 121, and green light
35   when voltage is applied between conductive layers 121 and 122.
To emit red light, a voltage is applied between conductive
layer 123 and metal contact layer 130 so that second blue

light emitting layer 115 emits blue light, which is then
converted to red light by red downconversion phosphor layer
114. Blue light emitted from second blue light emitting layer
115 is not permitted to pass through mirror structure 125 and
5 therefore resonates between layers 125 and 130, thereby
causing the efficient pumping of red downconversion phosphor
layer 114. The resulting emission of red light passes through
light emitting layers 113 and 112 and into substrate 111. The
configuration shown in Fig. 25 permits the more efficient
10 emission of red light than is possible with the use of red
organic light emitting layers.

In the embodiment shown in Fig. 25, substrate 111 is a
substantially transparent material, such as glass, quartz,
15 sapphire or plastic. For simplicity, the light emitting
layers 112, 113 and 115 are shown as single layers in the
drawing. As is well-known in the art, however, these layers
actually comprise multiple sublayers (e.g., HTL's, EL's and
ETL's) when they are not single-layer polymer devices. The
20 arrangement of the sublayers obviously depends on whether the
device is of DH (double heterostructure) or SH (single
heterostructure) configuration.

Where a transparent, conductive layer serves as both cathode
25 for one light emitting layer and anode for another, such as
layer 121, it preferably comprises indium-tin-oxide ("ITO").
Where a transparent, conductive layer does not serve as both
cathode and anode, such as layer 122, which serves as cathode
for green light emitting layer 113 but is separated from
30 second blue light emitting layer 115 by mirror structure 125,
it preferably comprises a compound electrode such as a
semi-transparent low work function metal and ITO. An anode
layer that does not serve as both cathode and anode, however,
is nonetheless preferably ITO. Metal contact layer 130
35 comprises any suitable material, such as magnesium, lithium,
aluminum, silver, gold and alloys thereof.

In another embodiment of the invention, green downconversion
phosphor layer 126 is inserted between red downconversion
phosphor layer 114 and second blue light emitting layer 115,
as shown in Fig. 26. Layer 126 results in the more efficient

5   conversion of blue to red light by the intermediate conversion
of blue to green light.

In another embodiment of the invention, blue light emitting
layers are used to pump both red and green downconversion

10   phosphor layers, as shown in Fig. 27. In device 200, a first
blue light emitting layer 112 is provided over substrate 111,
green downconversion phosphor layer 126 is provided over first
blue light emitting layer 112, second blue light emitting
layer 115 is provided over green downconversion layer 126, red

15   downconversion phosphor layer 114 is provided over second blue
light emitting layer 115, and third blue light emitting layer
127 is provided over red downconversion phosphor layer 114.
Disposed between the light emitting layers are transparent,
conductive layers 120, 121, 122, 123 and 125. Metal contact

20   layer 130 is provided over third blue light emitting layer
127. In addition, first and second mirror structures 128 and
125, respectively, are disposed between first blue light
emitting layer 112 and green downconversion layer 126, and
between second blue light emitting layer 115 and red

25   downconversion phosphor layer 114, respectively. First mirror
structure 128 permits the passage of red and green light while
blocking the passage of blue light. Second mirror structure
125 permits the passage of red light while blocking the
passage of green and blue light.

30
As representative embodiments of the subject invention in
which the OLED further includes a downconversion phosphor
layer, such an OLED may be comprised of: a transparent
substrate; a first blue organic light emitting layer over said

35   substrate; a green organic light emitting layer over said
first blue organic light emitting layer; a mirror structure
over said green organic light emitting layer, said mirror

structure comprising a multilayer stack of at least one
dielectric material, said mirror structure allowing the
passage of red light and blocking the passage of blue and
green light; a red downconversion phosphor layer over said
5   mirror structure; and a second blue organic light emitting
layer over said red downconversion phosphor layer.

Such an OLED containing a downconversion phosphor layer may,
alternatively, be comprised of: a transparent substrate; a
10   first blue organic light emitting layer over said substrate; a
first mirror structure over said first blue organic light
emitting layer, said mirror structure comprising a multilayer
stack of at least one dielectric material, said mirror
structure allowing the passage of red and green light and
15   blocking the passage of blue light; a green downconversion
phosphor layer over said first mirror structure; a second blue
organic light emitting layer over said green downconversion
phosphor layer; a mirror structure over said second blue
organic light emitting layer, said mirror structure comprising
20   a multilayer stack of at least one dielectric material, said
mirror structure allowing the passage of red light and
blocking the passage of blue and green light; a red
downconversion phosphor layer over said mirror structure; and
a third blue organic light emitting layer over said red
25   downconversion phosphor layer.

The light emitting devices of the present invention optionally
comprises a layer 140 of low-loss, high refractive index
dielectric material, such as titanium dioxide (TiO_2), between
30   transparent conductive layer 120 and substrate 111. Layer 140
is especially preferred when transparent, conductive layer 120
is made from ITO, which is a high-loss material. The
refractive indexes for TiO_2 and ITO are approximately 2.6 and
2.2, respectively. Layer 140 therefore substantially
35   eliminates waveguiding and absorption in the ITO, the light
emitted from light emitting layers 112, 113 and 115 now being
easily transmitted through layer 140 and substrate 111.

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This invention will now be described in detail with respect
to showing how certain specific representative embodiments
thereof will be made, the materials, apparatus and process
steps being understood as examples that are intended to be
5 illustrative only.   In particular, the invention is not
intended to be limited to the methods, materials, conditions,
process parameters, apparatus and the like specifically
recited herein.

10   **EXAMPLES**
Prior to deposition of the organic films for the
representative OLEDs of the present invention, (100) Si
substrates may be cleaned by sequential ultrasonic rinses in
detergent solution and deionized water, then boiled in 1,1,1-
15 trichloroethane, rinsed in acetone, and finally boiled in 2-
propanol.   Between each cleaning step, the substrates may be
dried in high purity nitrogen.   The background pressure prior
to deposition is normally 7×10^{-7} torr or lower and the
pressure during the deposition is about 5×10^{-7} to 1.1×10^{-6}
20 torr.

I. IOLED with a protection layer

An IOLED structure (Fig. 1) was grown starting with the
thermal evaporation in vacuum of a 1000 Å thick cathode
25 consisting of 25:1 Mg-Ag alloy, followed by a 500 Å thick
aluminum *tris*(8-hydroxyquinoline) (Alq$_3$) electron transporting
and electroluminescent (EL) layer, and a 250 Å thick hole
transporting layer (HTL) of N,N'-diphenyl-N,N'-bis(3-
methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD).
30 Alternatively, IOLEDs employing 4,4'-bis[N-(1-napthyl)-N-
phenyl-amino]biphenyl (α-NPD) as the HTL were also fabricated,
with results similar to those obtained using TPD.   To protect
the fragile HTL from the sputter deposition of the top ITO
anode contact, either a 3,4,9,10-perylenetetracarboxylic
35 dianhydride (PTCDA) or a copper phthalocyanine (CuPc) film was
employed.

Typical organic deposition rates ranged from 1 Å/s to 5 Å/s
with the substrate held at room temperature. Finally, the top
ITO layer was deposited by RF magnetron sputtering of a
pressed ITO target in a 2000:1 Ar:O_2 atmosphere, and 5 mTorr
5   pressure. The RF power was 5W, which resulted in a deposition
rate of 200 Å/hour.

The forward bias current-voltage (I-V) characteristics of 0.05
mm^2 IOLEDs with PTCDA and CuPc PCLs, as well as of a device
10 with no PCL are shown in Fig. 2. Fig. 3 shows the light
intensity vs. current (L-I) response of the IOLEDs in Fig. 2.

An OLED was also prepared comprised of structure having the
following sequence of layers: an ITO layer/60Å PTCDA/500Å
15 NPD/500Å Alq_3/1000Å MgAg/500Å Ag and a similar OLED, but
without the PTCDA layer. The current vs. voltage of this
device is shown in Fig. 5.

II.   OLEDs fabricated with improved ITO deposition method
20 In a representative example of the present invention in which
the improved ITO deposition method was used, a commercially
available glass substrate precoated with ITO, from Southwall
Technologies, Inc., Palo Alto, California, USA, was used. A
hole transport layer comprised of about 300 Å of TPD was
25 deposited onto the ITO anode layer, an electron transporting
layer comprised of about 500 Å of tris-(8-hydroxyquinoline)
aluminum(Alq_3)was deposited onto the TPD hole transporting
layer and a cathode layer of about 120 Å Mg-Ag was deposited
onto the Alq_3 electron transporting layer.
30
An ITO layer according to the present invention was then
prepared by depositing about 150 Å of ITO using only 5W of RF
power in the presence of about 200 sccm Ar and 0.1 sccm O_2 onto
the MG-Ag cathode layer and then an additional 400 Å of ITO
35 was deposited using 45W RF power in the presence of about 200
sccm Ar and about 0.42 sccm O_2.

Fig. 7 shows the current-voltage (I-V) characteristics of this
heterostructure. There was no practically discernible
difference between the I-V characteristics of this device as
compared with an OLED having the entire ITO layer deposited at
5 the slower deposition rate.

Although the particular OLED structure of Fig. 6 has been
described, it is to be understood that any OLED structure
having an ITO layer deposited using a low initial deposition
10 rate and then a substantially higher deposition rate would be
in accordance with this invention.

III. OLEDs with an electron transporting layer containing an
organic free radical
15   1. A single heterostructure containing an organic free
radical.
A transparent substrate, is pre-coated with an indium tin
oxide (ITO) layer having a sheet resistance of about 15
Ω/square. The substrate may be ultrasonically cleaned in
20 detergent, followed by thorough rinsing in deionized water,
1,1,1-trichloroethane, acetone and methanol, and dried in pure
nitrogen gas between each step. The clean dry substrate is
then transferred to the vacuum deposition system. All organic
and metal depositions may then be carried out under high
25 vacuum ($< 2 \times 10^{-6}$ Torr). Depositions are carried out by thermal
evaporation from baffled Ta crucibles at a nominal deposition
rate of 2-4 Å /s. First, an approximately 350 Å layer of N,N'-
diphenyl-N,N'-bis(3-methyphenyl)-1,1-biphenyl-4,4'-diamine
(TPD) may be vapor deposited on the cleaned ITO substrate. A
30 sample of $M(C_5Ph_5)_2$, (where M may be Ge or Pb) may then be
heated to ca. 250°C, liberating $Cp^{\oplus \cdot}$, which may be deposited as
a layer on top of the TPD film. The final thickness of the
$Cp^{\oplus \cdot}$ film may be about 400 Å. An array of circular 250 mm
diameter 1,000 Å electrodes of approximately 10:1 Mg:Ag atomic
35 ratio may be subsequently deposited by co-evaporation from
separate Ta boats. A 500 Å thick layer of Ag may be deposited
to inhibit atmospheric oxidation of the electrode.

2.   A double heterostructure containing an organic free
radical

A double heterostructure may be fabricated by including a
5   separate emissive layer, which may be formed as doped or un-
doped tris-(8-hydroxyquinoline) aluminum Alq_3. The double
heterostructure may be prepared substantially as described for
the single heterostructure structure, except that after
depositing the TPD layer and before depositing the organic
10 free radical layer, a separate emissive layer of Alq_3 is
deposited.

IV. OLEDs with alternative host and/or dopant materials

In these particular embodiments, in which the alternative host
15 and/or dopant materials of the present invention were prepared
and incorporated into an OLED, the hole transport layer was
comprised of N,N'-diphenyl-N,N'-bis(3-methylpheny)1-1'biphenyl-
4,4'diamine (TPD), and the electron transporting layer was
comprised of the doped or undoped tris-(5-hydroxyquinoxaline)
20 aluminum (Alx_3) or of doped or undoped Alq_3.

The hole transporting material TPD and the electron
transporting materials Alq_3 and Alx_3 were synthesized according
to literature procedures, and were sublimed before use.
25

The dopant C_{60} was purchased from Southern Chemical Group, LLC,
and used as received.

The bisphenol-squarilium dopant of formula XI and the indigo
30 dye compound dopant were purchased from Aldrich Chemical Co.,
Inc., and sublimed twice to give the pure green and purple
crystalline materials, respectively.

Aluminum tris(5-hydroxyquinoxaline), (Alx_3), was prepared by
35 the reaction of aluminum trisisopropoxide with 5-
hydroxyquinoxaline in isopropanol under argon. Isopropanol

was dried over CaH$_2$ before use. The amount of the ligand taken
for the reaction was in slight excess. The isopropanol
mixture was refluxed under argon for one and a half hours, and
orange product was isolated by rotarvaporization.

5

Gallium tris(5-hydroxyquinoxaline), (Gax$_3$), was formed by
mixing 200 ml water solution of 0.2g Ga(NO$_3$)$_3$•xH$_2$O and an excess
of 1% alcoholic solution of the ligand at 60°C, followed by
10% ammonium hydroxide addition to make the solution slightly
10 basic. Orange precipitate was obtained, and, after cooling,
filtered off. The Gax$_3$ preparation was similar to that
described in *Spectrochimica Acta, 1956, Vol. 8, pp.1-8.*

For the reagents, 5-hydroxyquinoxaline was prepared according
15 to *S.K. Freeman, P.E. Spoerri, J. Org. Chem., 1951, 16, 438;*
aluminum trisisopropoxide (99.99% purity) and Ga(NO$_3$)$_3$•xH$_2$O
(99.999% purity) were bought from Aldrich Chemical Co.; and
isopropanol was obtained from Fisher Scientific.

20 The ITO/Borosilicate substrates (100Ω/square) were prepared
using standard procedures. All the chemicals were resistively
heated in various tantalum boats. TPD was first deposited at
a rate from one to four Å/s. The thickness was typically
controlled at about 300 Å.

25

The electron transporting layer (Alq$_3$, Alx$_3$) was doped with
various dyes (C$_{60}$, the bisphenol squarilium dye and the indigo
dye compound of formula IX). Typically, the dopant was first
vaporized with the substrates covered. After the rate of the
30 dopant was stabilized, the host material was vaporized at the
prescribed rate. The cover over the substrates was then
opened and the host and guest were deposited at the desired
concentration. The rate of dopant was normally 0.1 - 0.2 Å/s.
The total thickness of this layer was controlled at about 450
35 Å.

The substrates were then released to air and masks were put
directly on the substrates. The masks are made of stainless
steel sheet and contain holes with diameters of 0.25, 0.5,
0.75, and 1.0 mm. The substrates were then put back into
5   vacuum for further coating.

Magnesium and silver were co-deposited at a rate normally of
2.6 Å/s. The ratio of Mg:Ag varied from 7:1 to 12:1. The
thickness of this layer was typically about 500 Å. Finally,
10 1000 Å Ag was deposited at the rate between one to four Å/s.

The I-V characteristics of these OLEDs were measured and are
shown for the doped and undoped Alx_3 in Fig. 13. The close
similarity of the results with and without the dopant shows
15 that the dopant is not perturbing the electrical properties of
the device.

For the OLEDs containing an emissive electron transporting
layer of Alq_3 (as the host material with and without the same
20 fluorescent dye dopant, wherein the energy match between the
host material and the dopant was poor) nearly all of the EL
emission was obtained from the Alq_3.

V.   Preparation of a Compound of Formula XII wherein M = Ga
25 A 0.25-g sample of 4-hydroxypyrazolo[3,4-d]pyrimidine is
dissolved in 2.5 mL of aqueous 1.1 M NaOH. A solution prepared
by dissolving 0.114 g of gallium nitrate in 1.5 mL of water is
added slowly to the NaOH solution. A precipitate forms upon
addition of the gallium nitrate. The white precipitate was
30 isolated by filtration, washed twice with 5-mL aliquots of
ethanol, and air dried. The isolated product, when excited at
250 nm, has an emission maximum at 390 nm.

VI. Preparation of Compounds of Formula XIII

   1.   Preparation of tris(4-ethynilphenyl) amine
[N(C₆H₄CCH)₃]

A solution of aqueous KOH is prepared by dissolving 1.26 g
5   (0.0225 mol) in methanol. The KOH solution is added to a
solution of tris(4-trimethylsilylethynylphenyl)amine that was
prepared by adding 2.00 g (0.0038 mol) to 100 mL of
tetrahydrofuran (THF), creating an orange solution that was
stirred at room temperature for 3 hours. The small amount of
10 orange precipitate that formed was removed by filtering the
reaction mixture through Celite. The Celite was washed with
two 10-mL portions of THF. The solvent was removed from the
combined filtrates in vacuo leaving a gummy beige-orange
residue. The residue was triturated with 50 mL of methanol and
15 left to stir for one hour at room temperature.

The product corresponding to Formula XIII was obtained as an
orange powder that was collected, washed with 2 5-mL portions
of pentane and dried in vacuo. Two additional crops were
20 obtained from the filtrates in a similar manner, providing a
total yield of 0.746 g (63%). The emission characteristics of
the compound at an excitation wavelength of 346 nm, were as
follows:
          emission (solution):   430 nm
25   emission (solid):   517 nm

   2.   Preparation of tris(4-trimethylsilylethynil-
phenyl)amine
          [N(C₆H₄CCSi(CH₃)₃]
30

A 100-mL Schenk flask is charged with 1.8 g of
trimethylsilylacetylene, 15 mL of diethylamine, 2.0 g of
tris(4-bromophenyl)amine, 0.59 g of PdCl₂, 0.175 g of
triphenylphosphine and 0.032 of copper(II) iodide. The
35 reaction mixture is heated to reflux for 24 hours. The solvent
is removed in vacuo, and the residue extracted with 70 mL of
benzene, followed by 70 mL of diethylether. Both organic

extracts are filtered through alumina, combined and the
solvent removed *in vacuo*. The resulting solid has a melting
point of 155 - 158 °C and shows strong blue fluorescence.
Excitation at either 255 or 350 nm gives luminescence centered
5 at 402 nm.

VII. Preparation of an OLED containing an emissive material
according to Formula I

A transparent substrate (*e.g.* glass or plastic) is precoated
10 with an indium tin oxide (ITO) layer having a sheet resistance
of about 15 Ω/square. The substrate may be cleaned by
thorough rinsing in deionized water, 1,1,1-trichloroethane,
acetone and methanol, and dried in pure nitrogen gas between
each step. The clean, dry substrate is then transferred to
15 the vacuum deposition system. All organic and metal
depositions may then be carried out under high vacuum (< 2 x
10^{-6} torr). Depositions are carried out by thermal evaporation
from baffled Ta crucibles at a nominal deposition rate of 2-4
angstroms/second. First, an approximately 350 Å layer of
20 N,NI-diphenyl-N,N'-bis(3-methylphenyl)-1,11-biphenyl-4,41-
diamine (TPD) may be vapor deposited onto the cleaned ITO
substrate. A sample of a compound according to Formula XII
and a selected fluorescent dye are then heated in separate Ta
boats to deposit a film on top of the TPD film that is a
25 mixture of 0.1-10 mole % dye in the receiving compound
according to Formula XII. The emission color of the OLED will
be dictated by the luminescent properties of the dye itself,
and can span the entire visible spectrum by appropriate choice
of the dye. This mixed film according to the present
30 invention is deposited to a thickness of about 400 Å. An
array of circular, 0.25-mm diameter, 1000-Å electrodes of
approximately 10:1 Mg:Ag ratio may be subsequently deposited
by co-evaporation from separate Ta boats. A 500 Å-thick layer
of Ag may then be added to inhibit atmospheric oxidation of
35 the electrode.

VIII. Preparation of an OLEDs containing an emissive material
according to Formula XIII

A transparent substrate (e.g. glass or plastic) is precoated
with an indium tin oxide (ITO) layer having a sheet resistance
5   of about 15 ohm/square. The substrate may be cleaned by
thorough rinsing in deionized water, 1,1,1-trichloroethane,
acetone and methanol, and dried in pure nitrogen gas between
each step. The clean, dry substrate is then transferred to
the vacuum deposition system. All organic and metal
10   depositions may then be carried out under high vacuum (< 2 x
10^{-6} torr). Depositions are carried out by thermal evaporation
from baffled Ta crucibles at a nominal deposition rate of 2-4
angstroms/second. First, a sample of a compound according to
Formula XIII and a selected fluorescent dye are heated in
15   separate Ta boats to deposit a film on the cleaned substrate
that is a mixture of 0.1-10 mole % dye in compound II. The
emission color of the OLED will be dictated by the luminescent
properties of the dye itself, and can span the entire visible
spectrum by appropriate choice of the dye. This mixed film
20   according to the present invention is deposited to a thickness
of about 400 angstroms. Next a film of a suitable hole
blocking material is deposited, such as 100 Å of an oxadiazole
derivative (e.g. 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-
oxadiazole), followed by film of an electron transporting
25   material (ca. 300 Å) such as aluminumtris(8-hydroxyquinoline).
An array of circular, 0.25-mm diameter, 1000-Å electrodes of
approximately 10:1 Mg:Ag ratio may be subsequently deposited
by co-evaporation from separate Ta boats. A 500 Å thick layer
of Ag may then be added to inhibit atmospheric oxidation of
30   the electrode.

Those of skill in the art may recognize certain modifications
to the various embodiments of the invention, which
modifications are meant to be covered by the spirit and scope
35   of the appended claims.

What Is Claimed Is:

1.   An organic light emitting device comprising an electroluminescent layer between a pair of electrodes wherein a protection layer is present between said electroluminescent layer and at least one of said electrodes.

2.   The organic light emitting device of claim 1 wherein said electroluminescent layer is contained in a heterostructure for producing electroluminescence with said protection layer being between a hole transporting layer and an anode layer.

3.   The organic light emitting device of claim 2 wherein said heterostructure is a single heterostructure.

4.   The organic light emitting device of claim 2 wherein said heterostructure is a double heterostructure.

5.   The organic light emitting device of claim 1 wherein said protection layer is comprised of a perylene, naphthalene, isoquinoline, phthalocyanine or phenanthroline based compound.

6.   The organic light emitting device of claim 5 wherein said compound is 3,4,9,10-perylenetetracarboxylic dianhydride; a phthalocyanine compound; 3,4,7,8-naphthalenetetracarboxylic dianhydride; 3,4,9,10-perylenetetracarboxylic dianhydride; bis(1,2,5-thiadiazolo)-p-quinobis(1,3-dithiole); 1,4,5,8-naphthalenetetracarboxylic dianhydride;

where R = H, alkyl or aryl;

where R = H, alkyl or aryl;
a compound having the CA index name, bisbenzimidazo[2,1-a:1',2'-b']anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-10,21-dione;
a compound having the CA index name,
bisnaphth[2',3':4,5]imidazo[2,1-a:2',1'-a']anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-10,21-dione;
a compound having the CA index name, bisbenzimidazo[2,1-b:2',1'-i]benzo[lmn][3,8]phenanthroline-8,1-dione;
a compound having the CA index name,
benzo[lmn]bisnaphth[2',3':4,5]imidazo[2,1-b:2'1'-I][3,8]phenanthroline-9,20-dione;
or a substituted derivative of one of said compounds.

7.   The organic light emitting device of claim 6 wherein said protection layer comprises said 3,4,9,10-perylenetetracarboxylic dianhydride.

8.   The organic light emitting device of claim 5 wherein said protection layer comprises copper phthalocyanine.

9.   The organic light emitting device of claim 2 wherein said heterostructure contains an electron transporting layer comprised of an organic free radical.

10.   The organic light emitting device of claim 2 wherein said heterostructure for producing electroluminescence contains an emissive layer comprised of a host material and a dopant, said host material being comprised of a metal complex of (5-hydroxy)quinoxaline having the chemical structure of formula:

wherein if M is Al, Ga or In, then n = 3, and if M is Zn or Mg, then n = 2.

11. The organic light emitting device of claim 10 wherein said dopant is comprised of a bisphenyl-squarilium compound of formula:

wherein R_1, R_2, R_3 and R_4 are, independently of each other, an unsubstituted or substituted alkyl, aryl or heterocycle, and R_5 and R_6 are, independently of each other, an unsubstituted or substituted alkyl, aryl, OH or NH_2.

12. The organic light emitting device of claim 10 wherein said dopant comprises an indigo dye compound having a chemical structure of formula:

wherein X = NH, NR$_9$, S, Se, Te, or O, wherein R$_9$ is alkyl or phenyl, and R$_7$ and R$_8$ are, independently of each other, an unsubstituted or substituted alkyl or aryl group, a π-electron donor group or a π-electron acceptor group.

13. The organic light emitting device of claim 10 wherein said dopant comprises a fullerene compound.

14. The organic light emitting device of claim 2 wherein said heterostructure contains an emissive layer comprised of a host material and a dopant, said dopant being comprised of a compound of formula:

wherein R$_1$, R$_2$, R$_3$ and R$_4$ are, independently of each other, an unsubstituted or substituted alkyl, aryl or heterocycle, and R$_5$ and R$_6$ are, independently of each other, an unsubstituted or substituted alkyl, aryl, OH or NH$_2$.

15. The organic light emitting device of claim 2 wherein said heterostructure contains an emissive layer comprised of a host material and a dopant, said dopant being comprised of an indigo dye compound of formula:

wherein X = NH, NR$_9$, S, Se, Te, or O, wherein R$_9$ is alkyl or phenyl, and R$_7$ and R$_8$ are, independently of each other, an unsubstituted or substituted alkyl or aryl group, a π-electron donor group or a π-electron acceptor group.

16. The organic light emitting device of claim 2 wherein said heterostructure contains an emissive layer comprised of a host material and a dopant, said dopant being comprised of a fullerene compound.

17. The organic light emitting device of claim 2 wherein said heterostructure contains an emissive layer comprised of a host compound represented by formula:

wherein M is an ion of a divalent or trivalent metal atom, wherein when M is trivalent, n = 3, and when M is divalent, then n = 2, wherein the metal atom is selected from the group consisting of aluminum, gallium, indium, and zinc, and wherein X, Y, and Z are each individually and independently C or N, such that at least two of X, Y and Z are N.

18. The organic light emitting device of claim 2 wherein said heterostructure contains an emissive layer comprised of a host compound having a structure represented by Formula:

$$N \left[\underset{}{\bigcirc} \!\!-\!\!\!\equiv\!\!-R \right]_3$$

wherein R is alkyl, phenyl, substituted alkyl, substituted
phenyl, trimethylsilyl, or substituted trimethylsilyl.

19. The organic light emitting device of claim 1 wherein said
organic light emitting device is included as one of a
plurality of organic light emitting layers in a stacked
arrangement; and a downconversion phosphor layer is disposed
between any two of said plurality of organic light emitting
layers.

20. The organic light emitting device of claim 1 wherein said
organic light emitting device is substantially transparent and
a low-reflectance absorber is arranged proximate to the
substantially transparent organic light emitting device so as
to form a high contrast light emitting display.

21. The use of the organic light emitting device of claim 1
in a panel display, vehicle, computer, television, printer,
wall screen, theater screen, stadium, electronic device,
lighting device, laser, screen billboard or sign.

22. An organic light emitting device comprising, in sequence,
        a substrate;
        a cathode layer;
        an electron transporting layer;
        a hole transporting layer;
        a protection layer; and
        an anode.

23.   The organic light emitting device of claim 22 wherein
said protection layer is comprised of a perylene, naphthalene,
isoquinoline, phthalocyanine or phenanthroline based compound.

24.   The organic light emitting device of claim 23 wherein
said compound is 3,4,9,10-perylenetetracarboxylic dianhydride;
3,4,7,8-naphthalenetetracarboxylic dianhydride; 3,4,9,10-
perylenetetracarboxylic dianhydride; bis(1,2,5-thiadiazolo)-p-
quinobis(1,3-dithiole); 1,4,5,8-naphthalenetetracarboxylic
dianhydride;

where R = H, alkyl or aryl;

where R = H, alkyl or aryl;
a compound having the CA index name, bisbenzimidazo[2,1-
a:1',2'-b']anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-10,21-
dione;
a compound having the CA index name,
bisnaphth[2',3':4,5]imidazo[2,1-a:2',1'-a']anthra[2,1,9-
def:6,5,10-d'e'f']diisoquinoline-10,21-dione;
a compound having the CA index name, bisbenzimidazo[2,1-
b:2',1'-i]benzo[lmn][3,8]phenanthroline-8,1-dione;

a compound having the CA index name,
benzo[lmn]bisnaphth[2',3':4,5]imidazo[2,1-b:2'1'-
I][3,8]phenanthroline-9,20-dione;.
or a substituted derivative of one of said compounds.

25. The organic light emitting device of claim 24 wherein
said protection layer comprises said 3,4,9,10-
perylenetetracarboxylic dianhydride.

26. The organic light emitting device of claim 23 wherein
said protection layer comprises copper phthalocyanine.

27. A method of fabricating an organic light emitting device
for producing electroluminescence comprising:
        fabricating a heterostructure for producing
    electroluminescence, wherein the fabrication process
    includes the step of depositing a protection layer on a
    hole transporting layer and then depositing an indium tin
    oxide anode layer on said protection layer.

28. The method according to claim 27 wherein said protection
layer is comprised of a perylene, naphthalene, isoquinoline,
phthalocyanine or phenanthroline based compound.

29. The organic light emitting device of claim 28 wherein
said compound is 3,4,9,10-perylenetetracarboxylic dianhydride;
3,4,7,8-naphthalenetetracarboxylic dianhydride; 3,4,9,10-
perylenetetracarboxylic dianhydride; bis(1,2,5-thiadiazolo)-p-
quinobis(1,3-dithiole); 1,4,5,8-naphthalenetetracarboxylic
·dianhydride;

where R = H, alkyl or aryl;

where R = H, alkyl or aryl;
a compound having the CA index name, bisbenzimidazo[2,1-a:1',2'-b']anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-10,21-dione;
a compound having the CA index name, bisnaphth[2',3':4,5]imidazo[2,1-a:2',1'-a']anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-10,21-dione;
a compound having the CA index name, bisbenzimidazo[2,1-b:2',1'-i]benzo[lmn][3,8]phenanthroline-8,1-dione;
a compound having the CA index name, benzo[lmn]bisnaphth[2',3':4,5]imidazo[2,1-b:2'1'-I][3,8]phenanthroline-9,20-dione;
or a substituted derivative of one of said compounds.

30.   The method according to claim 29 wherein said protection layer is comprised of said 3,4,9,10-perylenetetracarboxylic dianhydride.

31.   The method according to claim 28 wherein said protection layer comprises copper phthalocyanine.

32.   The method according to claim 27 wherein the fabrication process includes the steps of:
        (a)   depositing indium tin oxide at a low deposition rate to form a protective indium tin oxide layer; and then
        (b)   depositing indium tin oxide at a substantially higher deposition rate.

33. The method according to claim 27 wherein the fabrication process includes the step of heating an organometallic complex under vacuum conditions to a temperature sufficient to cause the organometallic complex to form organic free radicals from the gas phase to form an electron transporting layer.

34. The method according to claim 27 wherein the fabrication process includes the step of depositing a layer comprised of a host material and a dopant, said dopant being comprised of a compound of formula:

wherein R_1, R_2, R_3 and R_4 are, independently of each other, an unsubstituted or substituted alkyl, aryl or heterocycle, and R_5 and R_6 are, independently of each other, an unsubstituted or substituted alkyl, aryl, OH or NH_2.

35. The method according to claim 27 wherein the fabrication process includes the step of depositing a layer comprised of a host material and a dopant, said dopant being comprised of an indigo dye compound of formula:

wherein X = NH, NR_9, S, Se, Te, or O, wherein R_9 is alkyl or phenyl, and R_7 and R_8 are, independently of each other, an

unsubstituted or substituted alkyl or aryl group, a π-electron donor group or a π-electron acceptor group.

36. The method according to claim 27 wherein the fabrication process includes the step of depositing a layer comprised of a host material and a dopant, said dopant being comprised of a fullerene compound.

37. An organic light emitting device comprising a heterostructure for producing electroluminescence, wherein said heterostructure contains:

    (1)   an electron transporting layer comprised of an organic free radical;

    (2)   an emissive layer comprised of a host material and a dopant, said host material being comprised of a metal complex of (5-hydroxy)quinoxaline having the chemical structure of formula:

wherein when M is Al, Ga or In, n = 3, and when M is Zn or Mg, n = 2;

    (3)   an emissive layer comprised of a host material and a dopant, said host material being comprised of a compound of formula:

wherein R_1, R_2, R_3 and R_4 are, independently of each other, an unsubstituted or substituted alkyl, aryl or heterocycle, and R_5 and R_6 are, independently of each other, an unsubstituted or substituted alkyl, aryl, OH or NH_2;

(4)   an emissive layer comprised of a host material and a dopant, said dopant being comprised of an indigo dye compound of formula:

wherein X = NH, NR_9, S, Se, Te, or O, wherein R_9 is alkyl or phenyl, and R_7 and R_8 are, independently of each other, an unsubstituted or substituted alkyl or aryl group, a π-electron donor group or a π-electron acceptor group;

(5)   an emissive layer comprised of a host material and a dopant, said dopant being comprised of a fullerene compound;

(6)   an emissive layer comprised of a host material and a dopant, said host compound being represented by formula:

wherein M is an ion of a divalent or trivalent metal atom, wherein when M is trivalent, n = 3, and when M is divalent, then n = 2, wherein the metal atom is selected from the group consisting of aluminum, gallium, indium, and zinc, and wherein X, Y, and Z are each individually and independently C or N, such that at least two of X, Y and Z are N; or

(7)   an emissive layer comprised of a host material and a
dopant, said host compound being represented by formula:

wherein R is alkyl, phenyl, substituted alkyl, substituted
phenyl, trimethylsilyl, or substituted trimethylsilyl.

38.   A high contrast light emitting display comprising:
        a substantially transparent organic light emitting
device; and
        a low-reflectance absorber arranged proximate to the
substantially transparent organic light emitting device.

39.   A light emitting device comprising:

    a substrate;

    a plurality of organic light emitting layers in a stacked
arrangement over said substrate; and

    a downconversion phosphor layer disposed between any two
of said plurality of light emitting layers.

40.   A light emitting device comprising:

    a substrate;

    a filter structure over said substrate;

    a downconversion phosphor layer over said filter
structure; and

an organic light emitting layer over said downconversion
phosphor layer.
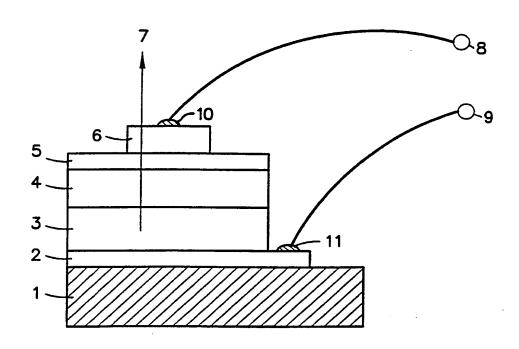
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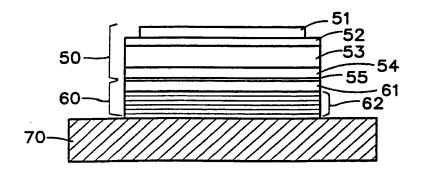
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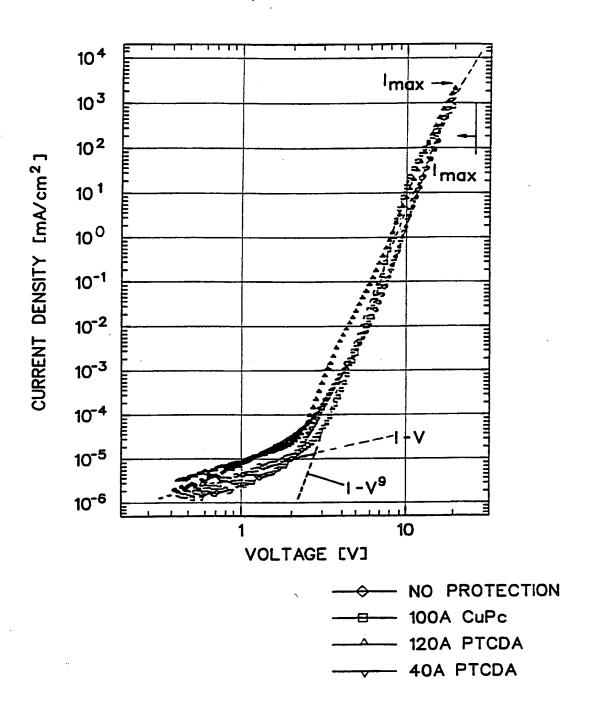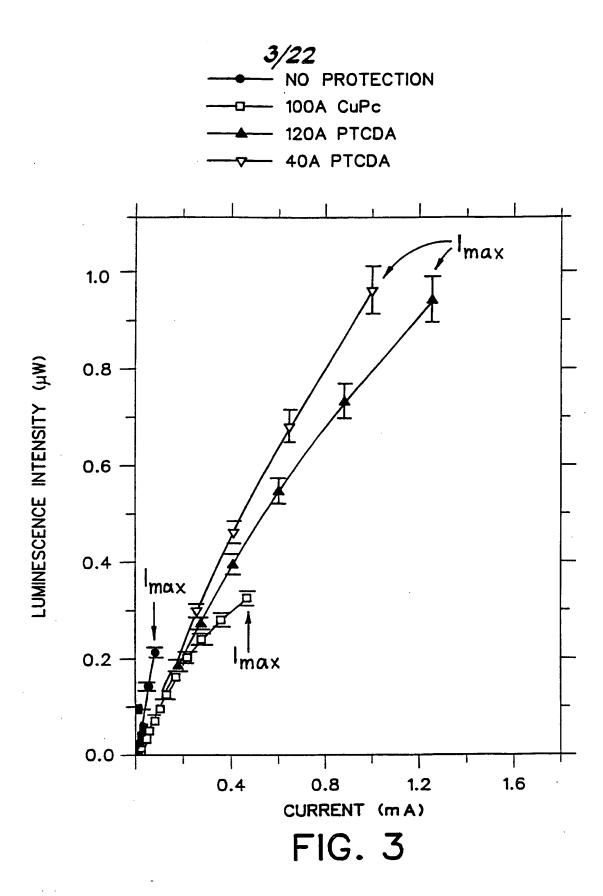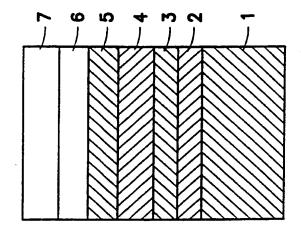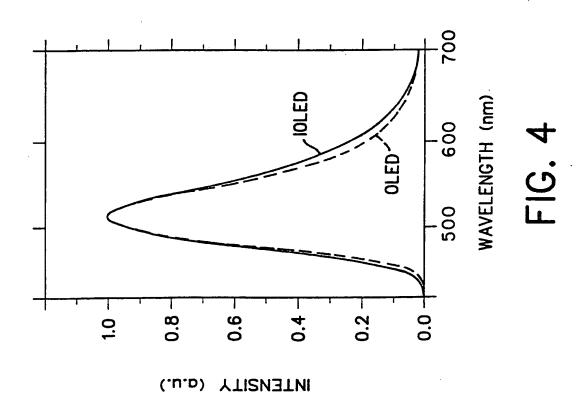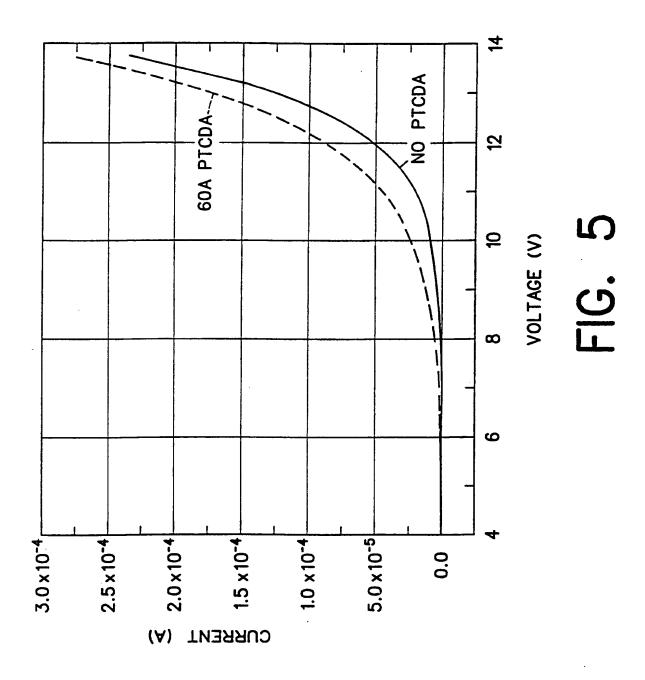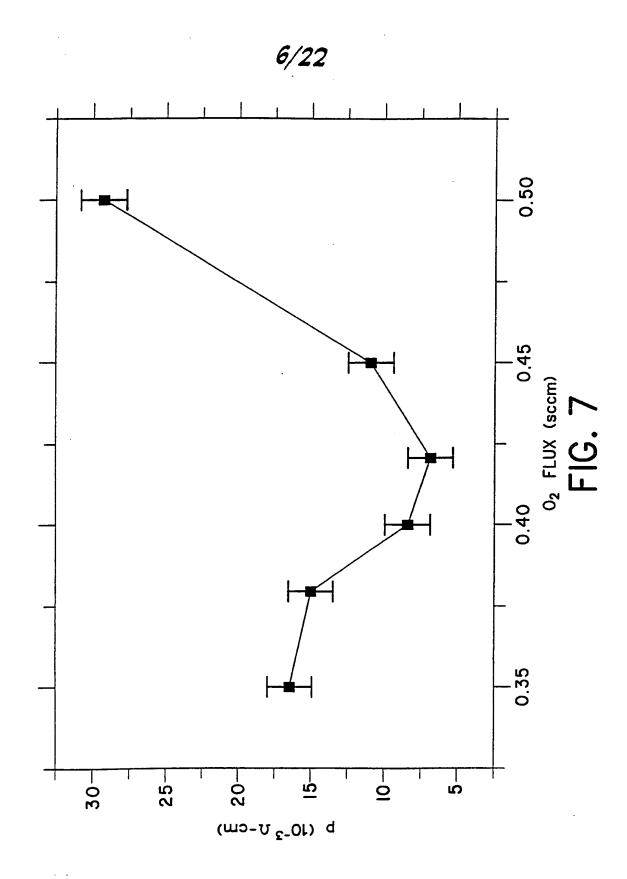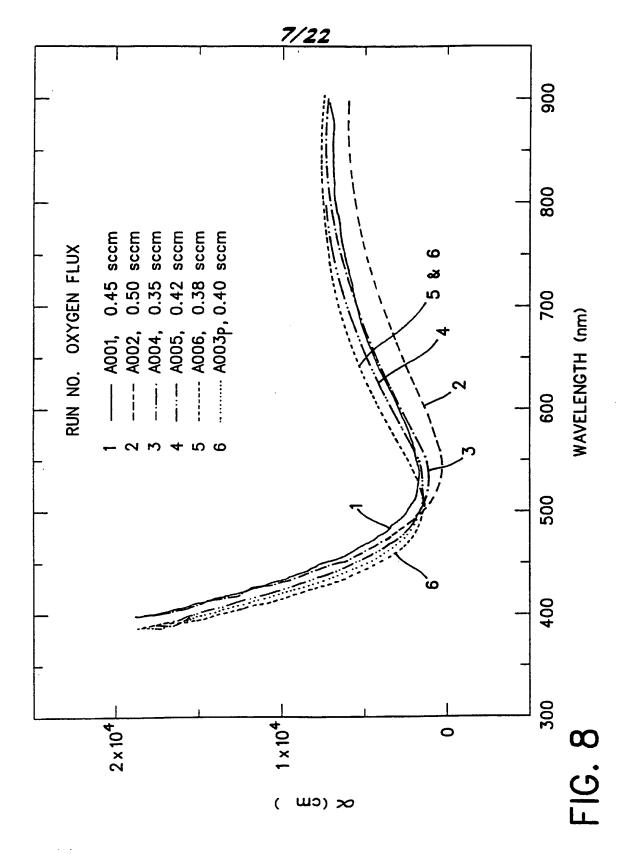
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FIG. 2

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FIG. 3

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FIG. 6

FIG. 4

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FIG. 5

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O₂ FLUX (sccm)

FIG. 7

P (10⁻³ Ω-cm)

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FIG. 8

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FIG. 9

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FIG. 10

FIG. 11

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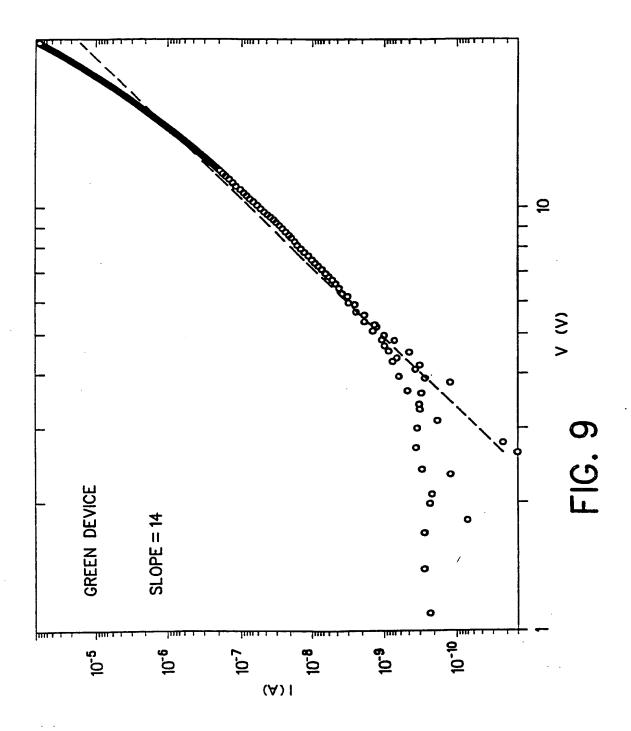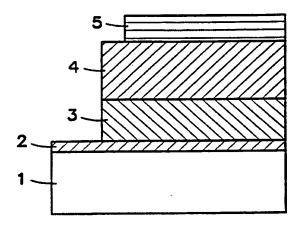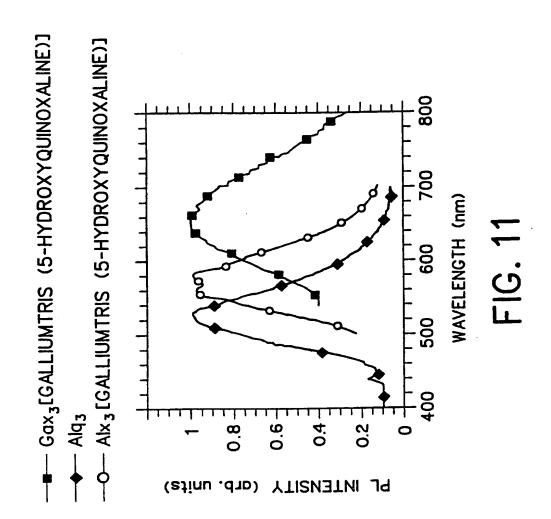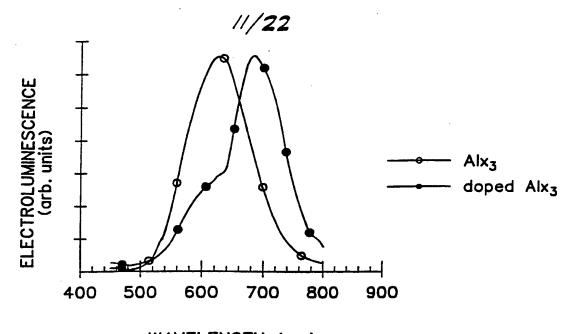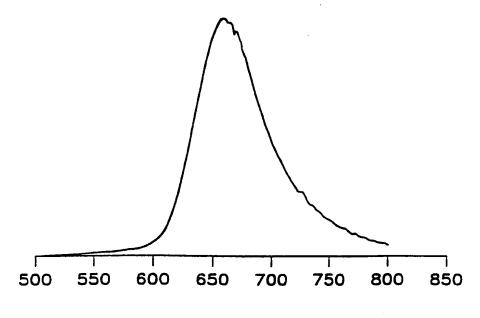
WAVELENGTH (nm)

FIG. 12

WAVELENGTH (nm)

FIG. 19
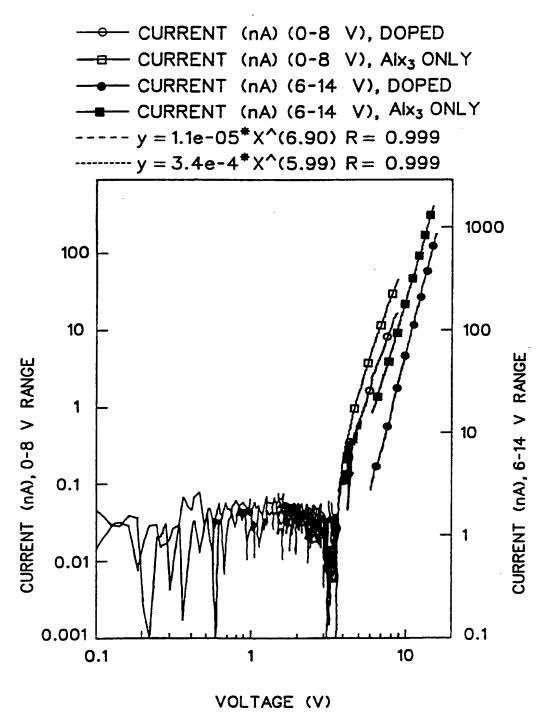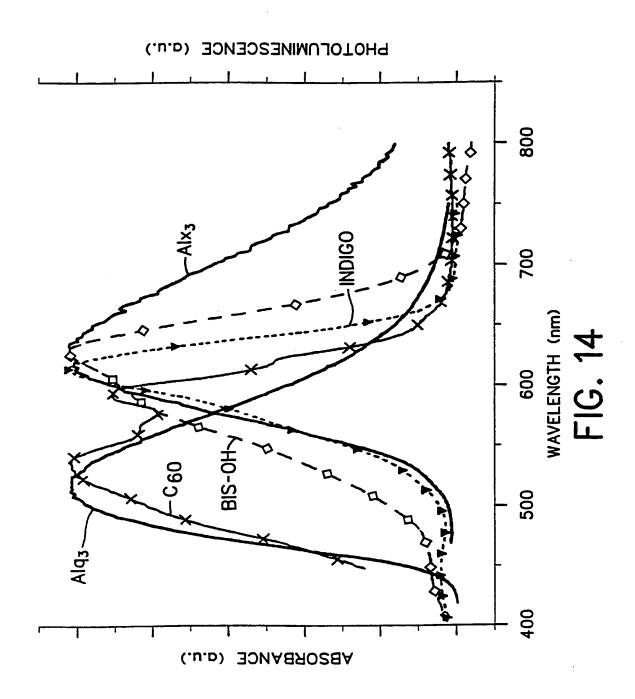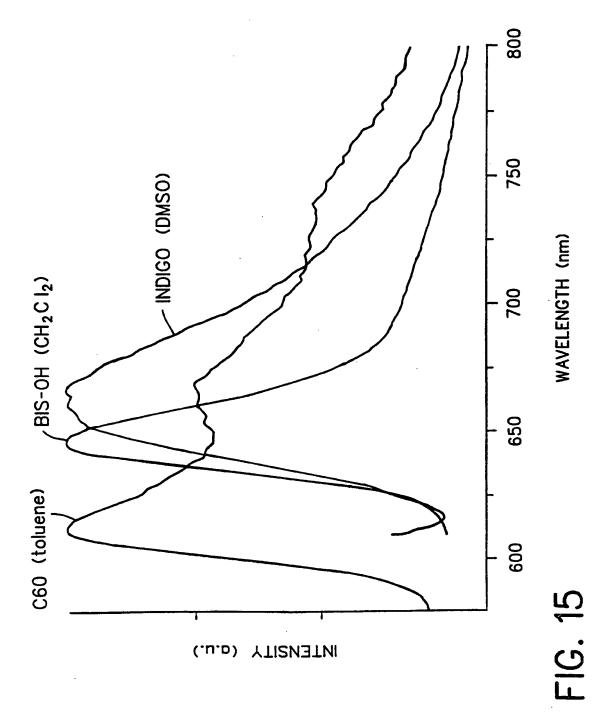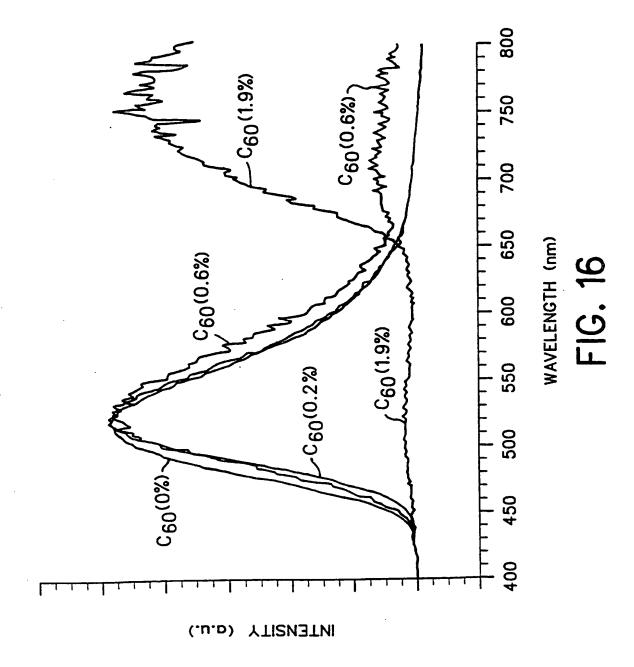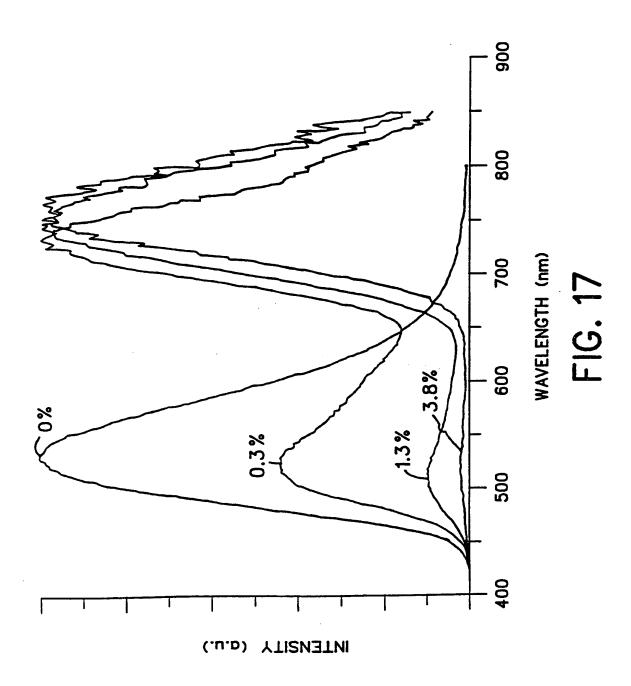
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FIG. 13

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FIG. 14

FIG. 15

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FIG. 16

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FIG. 17

FIG. 18

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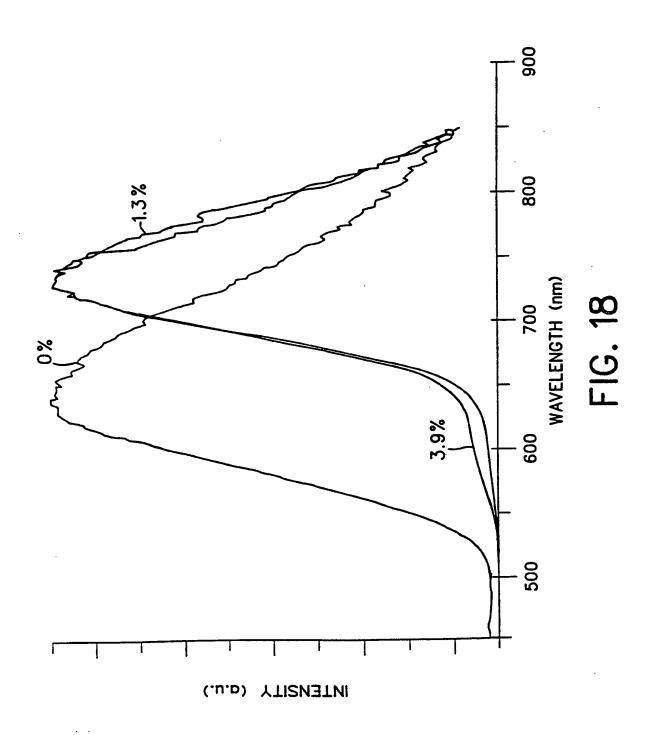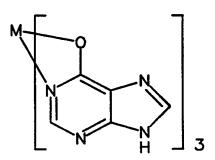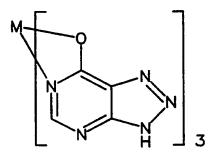
ligand = 4-hydroxypyrazolo(3, 4-d)pyrimidine

FIG.20a

ligand = hypoxanthine

FIG.20b

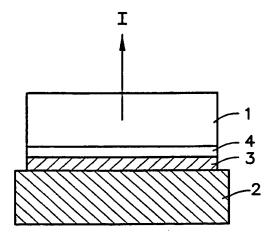ligand = azaguanine

FIG.20c

FIG.21
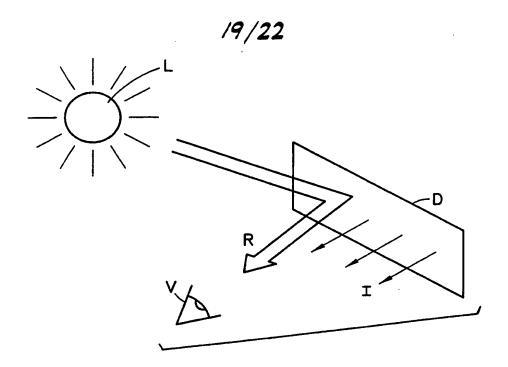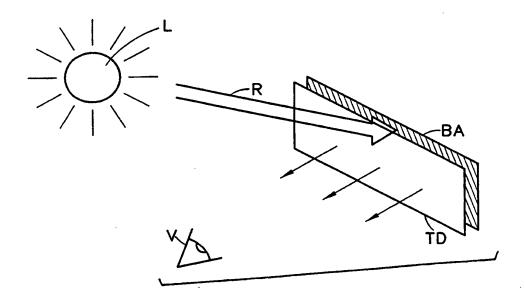
FIG.22
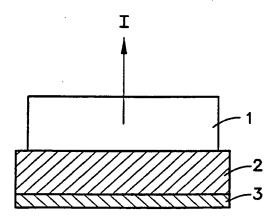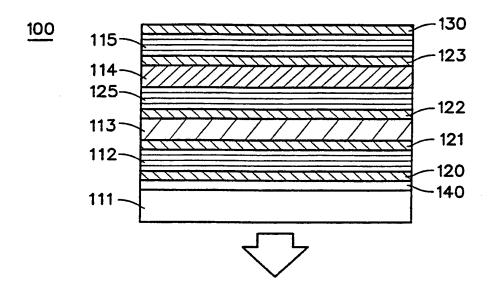
FIG.23

FIG.24

FIG.25
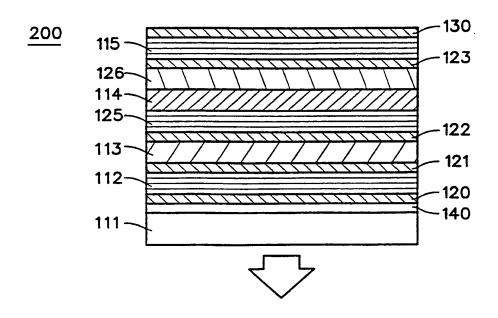
FIG.26
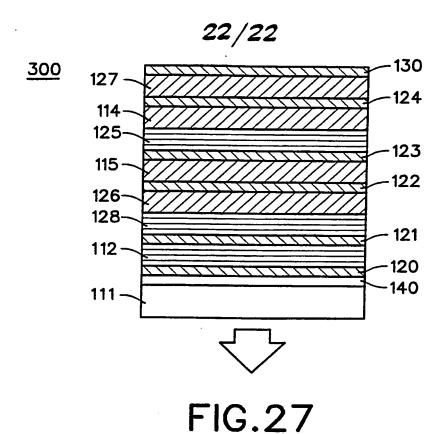
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FIG.27

FIG.28

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6)　:H01J 1/63; H05B 33/14

US CL　:313/504; 428/690; 450/122; 546/26, 28, 32, 37, 66; 549/232

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S.　:　313/504; 428/690; 450/122; 546/26, 28, 32, 37, 66; 549/232

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,950,950 A (PERRY ET AL.) 21 August 1990, whole document.	1-40

☐ Further documents are listed in the continuation of Box C.　　☐ See patent family annex.

*	Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	
"E"	earlier document published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	
		"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	
"P"	document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 MARCH 1998	27 APR 1998
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer RICHARD L. RAYMOND
Facsimile No.　(703) 305-3230	Telephone No.　(703) 308-1235

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